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REACTIONS OF CARBON-11 IN AROMATIC AND OXYGEN-CONTAINING ORGANIC COMPOUNDS

151

by

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TABLE OF CONTENTS

I. INTRODUCTION

A. Definition of Research Area

The reactions of recoil carbon atoms in aromatic and oxygen-containing organic compounds are discussed in this dissertation. The interpretation of these reactions is supplemented by the reactions of other recoil atoms and atoms generated at lower energies. The origin of recoil studies may be traced to Szilard and Chalmers (1) who first observed the chemical effects of a nuclear transformation in 1934. For their pioneering investigations the general field of hot atom studies is frequently termed Szilard-Chalmers chemistry.

The initial studies involved the neutron capture reaction of ^{127}I to produce the compound nucleus ^{128}I, a γ-emitter which recoils due to the emission process breaking its chemical bond and ultimately reacting to form ^{128}I-labeled compounds. This is in brief the fundamental process occurring in all recoil atom systems.

During the intervening 35 years a wide variety of recoil atoms have been generated by various techniques. The investigation of recoil halides produced many of the definitions and early reaction theories. It was proposed by Amaldi _et_ _al_. (2) and verified by Glueckauf and Fay (3) that recoil iodine produced by the (γ,n) reaction resulted in the same chemical behavior as the neutron capture reaction (4). This illustrates an important concept in recoil chemistry: if the recoil atom is generated at energies sufficiently large relative to chemical energies the chemical behavior of the atom as it undergoes energy degrading collisions is independent of the means of generation. Therefore accelerated ions (5, 6) neutralized before undergoing reaction behave as nuclear recoil atoms providing more flexible production methods. Recently recoil halogen research (7-12) has been extended to include studies of ^{38}Cl and ^{18}F. Recoil iodine chemistry has been reviewed by Willard (13) and Hornig and Willard (14).

Recoil tritium has been a second contributor to the background and terminology of recoil carbon chemistry. Significant reaction mechanisms include abstraction and replacement processes as well as the generation of reactive intermediates, tritium labeling of a variety of compounds, and isotope effects. Recent reviews of tritium chemistry should be consulted for a more complete discussion.

There appears to be no limit to the kinds of energetic atoms which can be studied in chemical systems. The only requirements are that the atom of interest be subject to extremely sensitive detection means (radioactive) and that isotopic exchange between the labeled atom and other atoms in the system does not interfere with product analysis. Recent studies include ^{32}P, metal atoms, S, and others in a wide range of chemical environments (15, 16). Such recoil studies are relevant to carbon studies, involve similar collision reactions, and must not be ignored by researchers in other recoil systems.

Recoil carbon atoms are the subject of this dissertation and a brief historical review will be presented. Two carbon isotopes meet the requirements of useful recoil atoms, ^{14}C discovered in 1941 by Ruben and Kamen (17) and first used in recoil studies in 1946 (18) and ^{11}C discovered by Yost et al. (19) in 1935 and first used for recoil investigations by Rowland and Libby in 1953 (20). Initial ^{14}C studies were concerned with surveying the product spectra produced by atomic carbon atoms in a variety of compounds with particular interest in the production of labeled compounds. The ^{14}C results and a discussion of its experimental form and limitations have been summarized by Wolf (21, 22). The usefulness of ^{14}C ($t_{1/2}$ = 5730 years) as a long lived label continues to be exploited in recent degradation studies to locate the position of the label in organic recoil products (21-23).

The utility of the shorter lived isotope, ^{11}C ($t_{1/2}$ = 20.4 min), was improved with the development of gas chromatography (24, 25) and its application to hot atom chemistry (26) which provided a means of rapid, quantitative separation of reaction products. Chromatographic separation with associated radiation detectors (27, 28) is now an intimate part of all hot atom research. The facile production of useful quantities of ^{11}C has provided a means of studying recoil carbon atoms in systems exposed to considerably reduced radiation doses compared with the long, destructive irradiations required in ^{14}C experiments.

B. Survey of Atomic Carbon Studies--a Reaction Approach

1. Physical approaches to recoil halogen studies

The first significant reaction model for recoil mechanisms was proposed by Libby (29) in 1947. A number of Szilard-Chalmers experiments had been reported for various organic halides determining the proportion of activity retained in the organic phase following a liquid extraction procedure, a quantity referred to as the organic retention. Typical organic retentions of 50% or more were dominated by labeled parent compound. Libby proposed a billiard-ball collision model assuming elastic collisions between the recoil atom and the bound atoms of parent molecules. If in the organic halide systems of interest large energy transfer occurred in collisions between the recoil atom and bound halogen atoms of the same mass the formation of a labeled parent molecule could result. On the other hand in collisions with low mass atoms the recoil atom would escape from the molecular fragment with slightly reduced energy. The collision model was extended (30) to include the interactions of lower energy (epithermal) atoms, presumed to be inelastic interactions, with molecules of the medium permitting the formation of nonparent organic molecules. This approach was in accord with the observations that reduced retention occurred in the vapor phase and in systems diluted with foreign molecules. Higher yields of nonparent molecules in the solid phase were attributed to the increased importance of epithermal reactions.

Modifications to Libby's approach were presented by Miller _et_ _al_. (31, 32) and by Capron and Oshima (33) in attempts to make the predicted trends quantitative. Their approaches were successful for selected data but were soon overwhelmed by additional experimental results.

Estrup and Wolfgang (34) assumed elastic collisions in a model for vapor phase reactions which are not complicated by complex cage effects. They expressed the total probability that a hot atom will react before losing its kinetic energy in terms of the average collisional energy loss and the efficiency of the reaction upon collision. The model predicted the relative effect of inert moderating compounds and provided a measure of the relative energy at which various products were formed. This theory was successfully tested (35) using experimental data on the effect of moderators upon reactions of hot hydrogen with methane. The theory was later extended (36) to binary systems of molecular reactants in which competition reactions occur. Recent discussions and applications of the Estrup-Wolfgang calculations (37-41) illustrate the importance of energy dependent reaction probabilities in sorting the relative significance of particular reactions at selected recoil energies.

As a parallel to this development various workers (42-44) questioned the assumption of elastic collisions, especially in the liquid phase, suggesting the important role of the molecular debris generated by the energy loss of the recoil atom. Willard proposed (45) a random fragmentation process in which the recoil atom undergoes inelastic collisions dissipating its energy in the formation of a variety of radicals along its cooling path. The nature and relative amounts of these radicals depend on the chemical composition of the medium, the energetics of reaction paths, and the density of the medium. The recoil atom finds itself in a pocket or nest of radicals with which it may react in a hot reaction or from which it may diffuse to react as a thermal atom. To identify thermal reactions Willard proposed operational criteria such as temperature and phase dependence and the effect of low concentrations of radical scavenging agents. Willard's approach rationalizes the wide variety of products observed, but the relative yields cannot be correlated with expected fragmentation patterns.

These physical-mathematical approaches faltered under the burden of additional data. The destructive blow was dealt by the results of Hornig *et al.* (43) in which a 50% gas phase yield of methyl iodide was reported for the methane system with recoil iodine and further inadequacies were demonstrated (46-48). The oversimplified physical approaches had given little regard to chemical considerations but stimulated interest in the experimental and theoretical aspects of hot atom chemistry. The development of chemically oriented reaction schemes has superceded these early models and provides insight to the understanding of the behavior of recoil atoms.

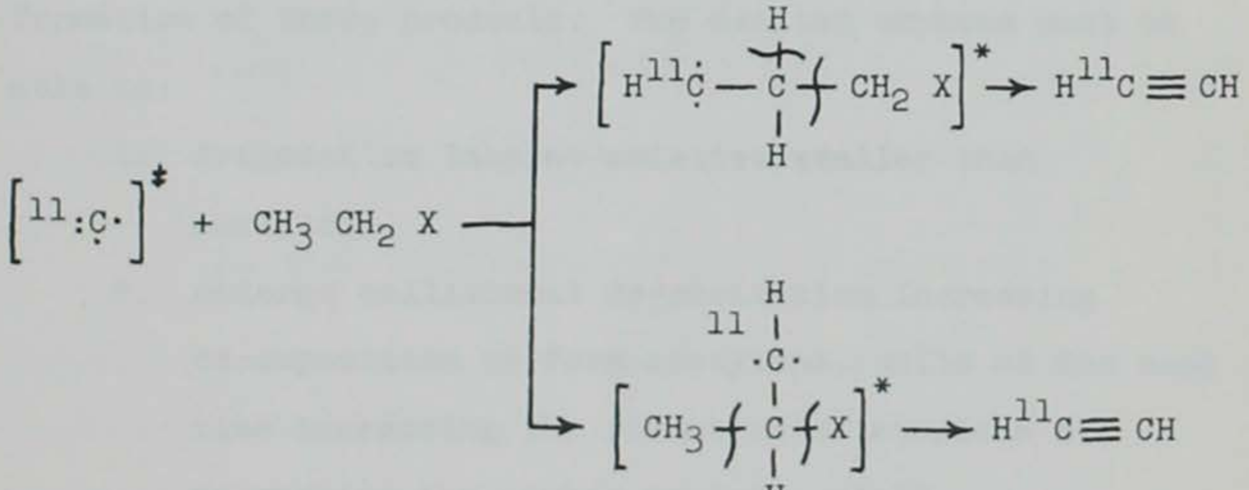
2. Insertion reactions

MacKay and Wolfgang (49) proposed carbon atom insertion into the C-H bonds as a primary mode of interaction with hydrocarbons. This simple process provides the first step in the reaction pathways leading to many of the observed products. The resultant adduct is formally a carbene which is definitely excited and not necessarily internally equilibrated. A variety of reaction alternatives is available to this intermediate including fragmentation to stable molecules such as acetylene and ethylene or into reactive species such as CH, CH_2, C_2H, C_2H_3, etc. Alternatively the insertion complex may be stabilized by rearranging to an alkene or may de-excite to react like a carbene generated by other means (50). The reaction pathway followed by a particular excited adduct depends upon its total energy, the distribution of this energy in the complex, and the rate of energy transfer to the surrounding molecules suggesting significant phase effects on the ultimate product distribution.

The high yield of acetylene from all the molecules containing carbon-hydrogen bonds studied to date prompted the initial insertion proposal by Wolfgang. Sufficient experimental evidence had been accumulated (22, 49, 51-54) to permit the development of statistical comparison based on insertion into various types of C-H bonds (55, 56). This bond counting and subsequent reactivity comparisons have played a significant role in the chemical understanding of carbon atom reactions with hydrocarbons.

The phase studies cited demonstrate that the insertion adduct formed in the reaction of a carbon atom with an alkane has a lifetime long compared with bond vibration frequencies and can collisionally deactivate. Conclusive evidence that bond energy effects change the excitation-decomposition sequence of the excited complex has been presented by Ache and Wolf (56). In addition it was shown that the lifetime is often long enough to permit hydrogen atom migration.

The acetylene produced from the specifically deuterated hydrocarbons $CD_3CH_2CH_3$, $CH_3CD_2CH_3$, $CD_3CH_2CD_3$ and from the deuterated alkyl halides CD_3CH_2X, CH_3CD_2X was the subject of valuable double labeling experiments (56). More than 85% of the acetylene produced was either isotopically pure C_2H_2 or C_2D_2 verifying intramolecular, localized formation. The alkyl halide series clearly demonstrated the increase in acetylene produced by the substituted methylene group compared with the methyl group in the series $CH_3CH_2CF_3$, CH_3CH_2F, CH_3CH_2Cl, CH_3CH_2Br, CH_3CH_2I. The increased acetylene yield parallels the decrease in energy required to free the acetylene moiety suggesting Wolf's mechanistic interpretation shown below.



The success of the insertion hypothesis is clear. It provides a convenient primary step that permits a variety of subsequent reaction paths which are affected by common chemical variables. The chemical mind finds this simple approach satisfying as the extensive use of insertion steps in recent hot atom mechanisms testifies.

The insertion mechanism is undoubtedly an over-simplification when reaction mechanisms are broken into more detailed processes. Serious doubt about the validity of the bond insertion process being the primary interaction of carbon atoms in the production of acetylene and ethylene from vapor phase hydrocarbons scavenged with oxygen has been generated by A. P. Wolf in recent publications. The pressure dependent yields of acetylene, ethylene, and carbon monoxide (57) reveal the multitude of reaction pathways which must be ascribed to the primary reaction intermediate if a single insertion carbene is assumed as the initial step in the formation of these products. The excited carbene must be able to:

1. fragment to labeled moieties smaller than acetylene,
2. undergo collisional de-excitation increasing decomposition to form acetylene, while at the same time increasing the formation of ethylene but decreasing the carbon monoxide yield,
3. behave very differently from photochemically produced carbenes, which do not show the increasing acetylene yield with increasing pressure (58-60).

The small fragments from 1 above must react with oxygen to form carbon monoxide. The most likely fragments are methyne and methylene. (Since $\cdots C\text{-}^{11}C\text{-}H$ bond formation is assumed in the carbene, carbon atoms are not expected to predominate.) Methylene is known to form both CO and CO_2 (61) but CO_2 is not observed here. Methyne is reactive with simple hydrocarbons (62) making CO formation in 4.5% O_2 mixtures unlikely. Clearly the single excited carbene proposed cannot display these diverse properties.

Welch and Wolf (57, 63) proposed the following model to accommodate the observed pressure trends.

$$^{11}C^{\ddagger} + RH \xrightarrow{k_1} [^{11}CRH]^* \tag{1}$$

$$[^{11}CRH]^* \xrightarrow{k_2} [\text{carbene intermediates}]^* \tag{2}$$

$$[^{11}CRH]^* \xrightarrow{k_3} {}^{11}C\ (\text{thermalized}) + [RH]^* \tag{3}$$

$$[^{11}CRH]^* + RH \xrightarrow{k_4} [\text{carbene intermediates}]^* + [RH]^* \tag{4}$$

$$[\text{carbene intermediates}]^* \longrightarrow \text{hot products} \tag{5}$$

The collision complex represented as $[^{11}CRH]^*$ is the pressure dependent precursor to the carbene intermediates and thermalized carbon atoms. Steps 2 and 3 compete as major reaction modes in low pressure systems. At higher pressures the formation of carbene intermediates is enhanced at the expense of reaction 3 resulting in increased yields of acetylene and ethylene but a decreased yield of carbon monoxide. Step 5 represents several reactions some of which are undoubtedly multi-step sequences.

Using this scheme a rate expression is derived which leads to an equation relating the yield of hot products to a function of k_2, k_3, k_4, and p (the probability that the carbon atom can react with the substrate to form a complex). The best values of these parameters are evaluated using the pressure dependent results giving an excellent fit to the data reported. The ratio k_2/k_3 is the ratio of collision complexes that do not need stabilization in order to react to those that produce thermalized carbon atoms unless collisionally stabilized. The fraction of collision complexes that needs stabilization decreases with increasing size of the hydrocarbon consistent with increased ability to absorb internal excitation energy. The lifetime of the collision complex which fragments to thermalized carbon is estimated by $1/k_3$ to be $\sim 10^{-9}$ seconds and increases with increasing hydrocarbon size.

The structure and physical nature of the collision complex $[^{11}CRH]^*$ has not been established although the existence of some intermediate preceding the insertion carbene is demanded by Wolf's results. It is difficult to extend his arguments to the liquid phase where collisional deactivation is rapid and relatively invariant making the distinction of intermediate steps obscure.

The significance of this modification of the primary insertion process has been demonstrated for particular gas phase systems. However no significant information is lost in most hot atom reaction mechanisms using the insertion species as the initial intermediate. The simplicity and effectiveness of the insertion hypothesis is justification for its application to the liquid phase recoil studies presented in this dissertation which have not been designed to investigate the detailed nature of reaction mechanisms.

3. Electrophilic reactions of carbon atoms

The nature of recoil carbon atom reactions has been attributed in large part to the voracious electrophilicity of the carbon atom. Atomic carbon lacks four of the electrons making up the normal valence shell and may be regarded as one of the most electron deficient of the simple neutral species ever studied. In addition to the C-H bond insertion reaction discussed previously common reactions include (64) insertion into C=C bonds and abstraction of hydrogen. These properties of the free carbon atom can be understood as an extrapolation of the properties of species deficient in two electrons, such as methylene, nitrenes, and atomic oxygen. The carbon atom shows less discrimination for attack at bonds as different as C-H and C=C and is unreactive toward C-C bonds. Inorganic π-bonded molecules present two potential reaction sites at which electrons can be shared with the carbon atom, the π-bond and nonbonding electron pairs commonly present on terminal atoms.

A wide variety of inorganic compounds have been investigated including (65-68) O_2, CO, CO_2, and SO_2 which yield ^{11}CO as the only significant product. This is true even in liquid oxygen where there is no three-body restriction on CO_2 formation. The carbon atom is clearly attacking the oxygen atom from the nonbonded side in these molecules. With N_2, N_2O, and NO (65) the carbon atom attacks the electron pairs of either nitrogen or oxygen to form ^{11}CN or ^{11}CO.

The results of reactions of recoil carbon with fluorocarbons have been reported very recently and the implications of these studies are as yet not clear (69-71). No convincing evidence has been reported for insertion of carbenes (72) or carbon atoms in C-F bonds although the reactivity of fluorocarbons toward carbon atoms is comparable to that of hydrocarbons. Current data are consistent with the hypothesis that CF formation is the favored initial reaction of carbon atoms with perfluoroalkanes. It appears that the carbon atom perferentially attacks at sterically accessible points where electrons are most readily available.

Attack of atomic carbon at the oxygen atom of ethylene oxide was postulated by MacKay and Wolfgang (48) to account for the high yield of ^{11}CO. Large yields of carbon monoxide from a variety of oxygen containing organic molecules have been reported by Palino (73) in this laboratory. Interaction of the carbon atom with a lone pair of electrons on oxygen rather than a bonding pair between oxygen and its neighboring atoms was suggested. Additional studies to evaluate the importance of electron availability and other aspects of the deoxygenation process are part of this dissertation.

Carbon atom attack on the π-electrons of benzene to form various π-complexes has been suggested by Rose <u>et</u> <u>al</u>. (74) as a primary reaction in benzene. Ring insertion reactions have also been proposed as explanations of the broad distribution of products obtained from benzene and other aromatic compounds (46, 75). The availability of the aromatic electrons may be cited as a possible explanation of the high reactivity of benzene toward carbon atoms as well as its tenacious tendency to polymerize. The results of aromatic studies constitute a second part of this dissertation and mechanisms will be thoroughly discussed.

Throughout this discussion of the electrophilic character of carbon atoms no clear distinction has been attempted between recoil and thermal atoms. Evaluation of the reactivity of thermal carbon continues to be an active research area with contradictory results reported. Marshall <u>et</u> <u>al</u>. (76) found that in highly moderated vapor phase ethylene both hot and thermal carbon atoms reacted by similar modes with the thermal species showing more discrimination favoring π-bond to C-H bond attack. No temperature effect was observed suggesting that both types of reactions had very low activation energies. Thermal carbon atoms form relatively low-energy adducts with ethylene which are rapidly de-excited in the solid phase diminishing fragmentation of the adducts resulting in small yields of acetylene.

Skell and Engel have generated active carbon species using a carbon-arc technique (77, 78) and have studied a wide variety of compounds. Reference will be made only to those recent publications which deal directly with the reactivity of carbon atoms and cite previous references too numerous to mention. Simultaneous deposition of carbon vapor with oxygen containing molecules at -196° C produces large yields of carbon monoxide (79, 80). Insertion into the double bonds of olefins is reported to produce allenes, a reaction ascribed to the excited ^1S state of carbon (81). Insertion into C-H and O-H bonds by C_1 species (80) occurs with the OH/CH insertion ratio nearly constant on a per bond basis for a series of simple alcohols. These results are of particular interest in the deoxygenation section of this dissertation.

There has been considerable interest in the extent to which the reactions of vapor deposited carbon may be attributed to free carbon atoms (82-85). The possibility that the carbon vapor studies involve intermediate complexes acting as carbon atom donors cannot be excluded and may account for the lack of quantitative agreement in product yields between thermalized recoil carbon and carbon vapor studies. The overall reactivity of the carbon atom may be seriously influenced by surface phenomena.

Other means of generating low energy carbon atoms are being examined to aid in the study of thermal reactions including photolysis of carbon suboxide (86), pulsed radiolysis (87), flash photolysis (62), and hot wire methods (88). Carbon vapor studies with benzene have been reported by Sprung _et_ _al_. (85) with the production of toluene and cycloheptatriene.

Martinotti _et_ _al_. (89) have reported some reactions of carbon atoms produced by decomposing [2-^{14}C]-carbon suboxide (C_3O_2) in a discharge flow system. Rate constants for several reactions were determined including recombination ($C + C$, $k = 1.3 \times 10^{10}\ \ell\ \text{mole}^{-1}\text{sec}^{-1}$), reaction with oxygen ($C + O_2$, $k = 1.5 \times 10^{9}$), and with methane, ethylene, and acetylene (k's $< 3.8 \times 10^{4}$). The relative inertness of hydrocarbons is startling. The carbon atoms were considerably more reactive toward radicals indicating that evaluation of the results of any carbon atom study must take into account not only the excitation state of the carbon but also the detailed composition and energy content of the substrate in which the carbon atom finds itself.

4. Reactions of other carbon species

Preliminary results of studies of energetic carbon atoms in inorganic solid matrices (90, 91) have been published. Evidence for trapped reactive species such as ^{11}CCl in alkali halides and carbon metal complexes in magnesium nitride has been presented including subsequent reactions of those species upon dissolution in various solvents. The entire field of carbon atom reactions is interdependent as attempts to explain the reactions occurring in a variety of systems at a wide range of carbon energies continue.

High energy collisions of carbon atoms with hydrogenous molecules produce partially hydrogenated carbon species by hydrogen abstraction and by the insertion-decomposition modes previously discussed. The methyne species was identified by Herzberg (92) by its absorption bands in the flash photolysis of diazomethane. Methyne reactions with ammonia were reported by Safrany et al. (93). Insertion of CH into C-H bonds has been cited as an explanation of part of the ethylene yield from hydrocarbons (53, 55, 94). The only steps required to produce ethylene following insertion into a methyl group are the rupture of one C-C bond and electronic rearrangement. Nicholas et al. (95) have attributed the formation of pentene-1 in hydrogen-ethylene mixtures to methyne via the allyl radical and addition to ethylene, but this result does not prove the involvement of methyne (49, 96). Reactions of methyne in the flash photolysis of methane have been reported by Braun *et al.* (62, 97). In recoil studies CH appears to undergo many reactions very similar to those of carbon atoms making it difficult in many cases to distinguish between them.

The chemistry of methylene has been reviewed by Kirmse (50). Methylene insertion reactions in alkanes were reported by Stoecklin and Wolf (53). Bond insertion ratios reported in the literature appear to depend on the source of methylene (98-100) indicating that several excited states are available in near thermal as well as in recoil studies.

Russel and Rowland (61) have recently reported methylene generated from doubly tritiated ketene and ^{14}C labeled ketene. The photolysis of these ketenes has revealed the formation of hydrogen, carbon monoxide, and carbon dioxide as reaction products of triplet methylene with oxygen via intermediates isoelectronic with O_3 (101, 102). The molecular hydrogen produced results from intramolecular elimination as verified by the formation of T_2. Application of the well studied reactions of methylene generated in low lying excited states to reactions of methylene in recoil reactions has proven difficult in view of the excitation energy present in these high energy reactions. The detailed behavior of methylene excited far above thermal and photochemical energies is difficult to elucidate.

Methyl radicals are produced in recoil carbon systems by hydrogen abstraction reactions which decrease the kinetic energy of the carbon species (21, 100, 103). In aliphatic hydrocarbons ~ 3% of the carbon atoms eventually appear as methyl radicals while in benzene much lower yields of methyl radicals reflect the reduced hydrogen availability. Thermal methyl radicals have commonly been scavenged by iodine present in the irradiated solution in radiolysis systems (104) as well as in recoil systems.

Scavenger effectiveness toward a wide variety of radicals, some at epithermal energies, has been investigated in several studies. Nicholas et al. (95) have observed the reactions of methylene in ethylene leading to methane, propane, and pentane. These products are replaced by methyl iodide if iodine is present at low concentration during the irradiation. Rack and Voigt (52) and Palino (73) have reported similar results finding a larger methyl iodide yield than can be explained by the decrease in methane yield and using this as evidence for reactions of methyl radicals in addition to the formation of methane. In a variety of systems they have reported significant yields of methane (e.g., ~ 4% methane from cyclohexane (52)) even in the presence of iodine indicating a reaction of hot methyl radicals which cannot be intercepted by radical scavengers. The work of Stoecklin and Wolf (53) and MacKay and Wolfgang (49) places a somewhat lower limit on epithermal methane formation in gaseous systems. Each of the carbo-hydrogen species produced in recoil systems exhibits properties not observed for these species produced by lower energy methods resulting in reaction products and mechanisms attributed to excess kinetic and excitation energy.

One of the major goals of hot atom studies is to determine the yields of all the labeled products, that is to account for 100% of the radioactive atoms produced. When that goal is approached in any particular system attempts to explain the complete product spectrum on the basis of reaction mechanisms are possible. The best example of such a system was presented by Palino and Voigt (28) who studied liquid methanol as pure and as iodine scavenged systems. Their product analysis accounted for more than 86% of the carbon atoms in pure methanol and more than 92% in the iodine scavenged case. In addition dose and dose rate dependences were determined for a number of products.

Detailed reaction schemes involving ^{11}C, ^{11}CH, $^{11}CH_2$, and $^{11}CH_3$ interactions with methanol molecules and radiation produced radicals were developed consistent with the observed yields, dose and scavenger effects, and reasonable hot carbon reactions. Additional product identification and mechanism investigations in the methanol systems are a part of this dissertation which will include discussions of their reaction scheme.

The use of iodine as a hydrocarbon radical scavenger has been cited several times in this introduction. A very recent paper by Johnsen et al. (105) discusses iodine as a scavenger in γ-irradiated hydrocarbons and hydrocarbon-alcohol solutions. Previously iodine has been added before irradiation and the hydrogen atom yield measured by the decrease in molecular hydrogen yield compared to that in the unscavenged hydrocarbon or directly by the yield of HI. The G(HI) in n-hexane-iodine mixtures has been reported by Meshitsuka and Burton (106) to be 2.5 by an extraction of HI which agrees well with Johnsen's G(HI) = 2.42 determined by converting HI to I_3^- by the addition of ethanol after the irradiation.

The dependence of measured hydrogen atom yield upon an ionic mechanism has been suggested as an alternative to the exclusive free radical mechanism (107). The yield $G(e^-)$ = 2.6 for scavengable electrons in n-hexane has been reported by Rajenbach and Kaldor (108) using perfluorobutane as an electron scavenger and an additional yield $G(H\cdot)$ = 1.4 using hexene as a radical trap. These results suggest that

I_2 is scavenging electrons rather than H atoms and HI is formed only subsequently. The presumed reaction scheme is then:

$$RH \rightsquigarrow RH^+ + e^- \rightarrow RH^* \rightarrow R\cdot + H\cdot^*$$

$$H\cdot + RH \rightarrow H_2 + R\cdot$$

and in the presence of iodine

$$I_2 + e^- \rightarrow I^- + I\cdot$$

$$I^- + RH^+ \rightarrow R\cdot + HI$$

Iodine reduces the molecular hydrogen yield by intercepting the electrons in the first reaction and ultimately results in the formation of HI without involving hydrogen atoms. This evidence for iodine as an efficient electron scavenger will be important in later discussions of the methanol system. A general discussion by Schuler (109) of the applicability of scavenger methods to free radical detection in organic systems with a resumé of various studies is suggested for additional information.

C. Final Introductory Comments

I have presented a brief discussion of the development of hot atom chemistry with particular emphasis on the elucidation of reaction mechanisms in carbon recoil chemistry. The interplay of insertion, abstraction, and free radical reactions generating intermediates with excitation energies much greater than those generated by other techniques distinguishes recoil carbon as an effective probe in novel high energy reactions. These studies serve as an extension of high temperature chemistry in the more general quest to understand the fundamental nature of all chemical reactions.

Certain limitations inherent in recoil studies are apparent from the reaction survey. The total energy deposited in a recoil system during the irradiation might suggest the production of utter chaos. Certainly radiation damage is significant and frequently the participation of radiation produced species can be elucidated, but the damage by no means renders recoil systems intractable. The lack of detailed information about energetic intermediates poses a problem more serious in recoil systems than in thermal systems since there is a lack of effective techniques.

The determination of labeled sites by degradation studies is a valuable asset in understanding the reaction mechanisms and the behavior of intermediates. Unfortunately degradation studies are limited to isotopes with half-lives sufficiently long to maintain measurable activities during the degradation sequence. For ^{11}C this allows little more than an hour putting severe restrictions on useful investigations. Double labeling studies using deuterium or tritium have been discussed previously and continue to be of considerable value.

Modern instrumental techniques for product identification and structure determination are difficult to apply due to the small quantities of labeled materials produced. The gas chromatograph has been invaluable as a means of rapid separation and product identification but this technique suffers from a lack of absolute identification and the possibility of incomplete separation. The studies presented in this dissertation were undertaken despite these limitations and with the hope of contributing to the development of recoil atomic chemistry.

D. Purpose of Investigation

Recoil carbon studies have been shown to be effective in elucidating interesting high energy reactions. All reaction mechanisms result from the accumulation of accurate data from well designed experiments and must withstand additional evaluative experiments. It is the purpose of this investigation to:

1. Accumulate copious data using proven techniques to determine the distribution of recoil carbon products in a series of aromatic compounds and in a selection of small oxygen-containing molecules,

2. Interpret the results for the aromatic compounds on the basis of reasonable reaction mechanisms using the methyl groups of toluene and para-xylene as marking groups to compare reactions with those observed for benzene. The extent of the analogies and the effects of the methyl groups are of particular interest,
3. Study the carbon monoxide formation process in a variety of alcohols and ethers. Previous results (73) reveal a strong dose dependence of the carbon monoxide yield from methanol and a systematic variation in yield with molecular structure for which a model has been proposed,
4. Identify additional products in the methanol systems to supplement the Palino and Voigt (28) analysis,
5. Evaluate the detailed reaction scheme and mechanisms proposed by Palino and Voigt (28) for methanol by observing the effects of selected compounds added prior to irradiation, and
6. Initiate studies of benzene-methanol mixtures to evaluate the yield and mechanism effects these two well-studied compounds have on each other. The ability of benzene to inhibit radiation damage in methanol is of particular interest.

II. EXPERIMENTAL

A. Materials and Equipment

The experimental aspects of this work closely parallel those of Palino (73) and frequent reference will be made to his detailed discussions. At the outset of my research it appeared beneficial to establish an experimental system similar to Palino's to facilitate direct comparison of results and capitalize on extensions of his work. I extend my appreciation to G. F. Palino for his cooperation and stimulating discussions during the preliminary stages of the work presented. It is hoped that the discussion presented here will be complete enough to provide the reader with details of the experiments sufficient to permit an accurate understanding of the results.

Table 1 lists the reagents used in irradiations, with pertinent data concerning their source and initial purity. Purification procedures were performed on several of these compounds (vide infra) to remove traces of impurities known or suspected as possible interferences. The purity of reagents used in these recoil studies was sufficient to insure reproducible results from samples prepared from multiple commercial lots. Samples of all reagents showed no detectable impurities before irradiation as evaluated by sensitive gas chromatographic analysis.

Benzene, toluene, para-xylene, and iso-pentane were

Table 1. Reagent source and purity data

Compound	Source and description	Purity (mole %)
Benzene	Phillips Petroleum Company Research Grade	99.94
Toluene	Phillips Petroleum Company Research Grade	99.97
para-Xylene	Phillips Petroleum Company Research Grade	99.90
Methanol	Fisher Scientific Company Fisher Certified Reagent	99.9^+
Ethanol	Enjay Chemical Company	99.99
n-Butanol	Matheson Coleman & Bell Chromatoquality	$99.^+$
sec-Butanol	Matheson Coleman & Bell Chromatoquality	$99.^+$
iso-Butanol	Matheson Coleman & Bell Chromatoquality	$99.^+$
tert-Butanol	Matheson Coleman & Bell Chromatoquality	$99.^+$
Propyl Ether	Matheson Coleman & Bell Reagent	not stated
iso-Propyl Ether	Matheson Coleman & Bell Chromatoquality	$99.^+$
Tetrahydrofuran	Matheson Coleman & Bell Chromatoquality	$99.^+$
iso-Propanol	Fisher Scientific Company Fisher Certified Reagent	$99.^+$
para-Dioxane	Matheson Coleman & Bell Chromatoquality	$99.^+$

Table 1. (Continued)

Compound	Source and description	Purity (mole %)
iso-Pentane	Phillips Petroleum Company Research Grade	99.99
Acetone	Matheson Coleman & Bell Chromatoquality	99.+
Iodine[a]	J. T. Baker Chemical Company sublimed Baker Analyzed Reagent	100.
DPPH[b]	Eastman Organic Chemicals	not stated

[a] Used as scavenger.

[b] 2,2-diphenyl-1-picrylhydrazyl; used as scavenger.

not subjected to laboratory purification in view of their high purity. Their hydrocarbon impurities would display negligible interference as a result of their statistical disadvantage and reactivities similar to the parent compounds.

The well-documented discussion by Palino (73, pp. 27-31) concerning the following purification procedures is recommended. Ethanol, iso-propanol, and the butyl alcohols were refluxed with 2,4-dinitrophenylhydrazine and sulfuric acid to remove traces of aldehydes and ketones as outlined by Baxendale and Mellows (110). The alcohols were then treated to remove traces of water using molecular sieves in the Soxhlet extractor designed by Palino. Methanol was freed of aldehydes and ketones by the same procedure but was dried by a procedure outlined by Fieser (111) using magnesium metal. This process is reported to reduce the water content of methanol to below 0.05%.

Propyl ether, iso-propyl ether, tetrahydrofuran, para-dioxane, and acetone were subjected to only minor purification involving a simple fractionation. The ethers were dried in a second fractionation using nonindicating Drierite in the vaporization flask and acetone was dried in the molecular sieves apparatus. The DPPH scavenger was recrystallized from chloroform-diethyl ether mixture and stored in vacuo.

The sample preparation procedure is discussed in detail by Palino. Briefly the procedure used was as follows. The purified reagent was manually transferred from the distillation apparatus to a small vacuum system. The reagent was frozen using an appropriate cooling bath (liquid nitrogen or a solid carbon dioxide-acetone slurry) depending on the vapor pressure of the reagent at -78° C and the system was evacuated. The reagent was permitted to thaw in a closed container to permit trapped vapors to escape from the liquid. This procedure was repeated until the vacuum system showed no measurable pressure over the frozen reagent. Using the vacuum transfer apparatus illustrated by Palino (73, p. 32) pyrex sample bulbs (8.6 ± 0.1 mm diameter) were filled by vacuum transfer and sealed. Scavenged samples were filled by pipetting and degassed individually by the technique discussed above with minimal exposure of the dried reagent to the atmosphere.

In this work an improved vacuum line was assembled utilizing a mercury diffusion pump to increase the pumping rate and provide more dependable operation at low pressures. The system pressure was rapidly reduced to less than one micron. Evidence for thorough degassing was obtained from the hydrocarbon samples by the absence of ^{11}CO activity. The reaction $^{11}C + O_2 \rightarrow {}^{11}CO$ for thermal atoms is an extremely sensitive test for dissolved oxygen in view of the reported (89) rate constant ($k = 1.5 \times 10^9 \ \ell \ \text{mole}^{-1} \ \text{sec}^{-1}$). The degassing procedure was performed using cooling solutions selected for particular reagents to provide low vapor pressures at maximum convenient temperatures. Use of solutions with equilibrium temperatures higher than liquid nitrogen (- 196° C) facilitated removal of dissolved oxygen and nitrogen which are near their own liquification points even under reduced pressure at liquid nitrogen temperature.

The model 5750 F & M Research Chromatograph used for the radiogas chromatographic analysis was modified to provide the capabilities of efficient sample injection with the options of simultaneous injection of liquid and gaseous carriers. The output of the chromatograph's thermal conductivity detector and a side-hole NaI(Tl) detector system was recorded on a dual pen model 7128A Hewlett-Packard strip chart recorder. The amplified signal from the NaI detector was analyzed by a Nuclear-Chicago Model 27352 Single Channel Analyzer adjusted to accept pulses corresponding to 0.4 to 1.2 MeV γ-rays. This permitted detection of the 0.511 MeV annihilation γ-rays of the ^{11}C positron as well as the 1.022 MeV sum peak while rejecting events of energies outside this range, thus reducing background and increasing the signal to noise ratio.

The objective was to compare the activity of any particular ^{11}C-labeled product with the total ^{11}C activity.

Digital output from the analyzer system was provided by a Nuclear-Chicago Model 8735 Digital Integrator. The digital integrator was used to print out the recorded activity accumulated by the analyzer during preset time intervals of 6 or 12 seconds for facile integration of product activity peaks. Diagrams of the radioactive effluent detector system and of the analysis system were presented by Palino (73, pp. 35-37).

The total sample activity was determined before injection onto the chromatograph column in a fixed geometry 8.0 cm above the crystal surface using the same crystal-analyzer system. This technique provides an accurate monitor for the total activity without introducing the complexity of two counting systems. The dependability and long term stability (vide infra) of the detector system provided continuous use during a 36 month period for the analysis of nearly 1,000 samples.

The columns used to effect the product separations were fabricated from 8 mm Pyrex tubing and ranged in length from 0.5 to 11.0 m. The column materials were prepared by dissolving the desired quantity of liquid phase in a suitable solvent, mixing it with the appropriate quantity of solid support, and evaporating the solvent using a flash evaporator. A listing of the columns used in this study appears in Table 2.

Table 2. Chromatographic columns used for product separations

Column description	
10 m - 35%	2-Ethylhexyl Acetate (Eastman Organic) on Chromosorb P[a]
4 m - 10%	Carbowax 20M (F & M Scientific) on Chromosorb W[b]
5 m - 20%	Igepal CO 880 (Analabs) on Anakrom[c]
11 m - 30%	Tripropionin (K & K Laboratories) on Chromosorb P
4 m - 30%	Triisovalerin (K & K Laboratories) on Chromosorb W
0.5 m - 10%	Carbowax 20M (F & M Scientific) on Chromosorb W
4 m - 35%	Tripropionin (K & K Laboratories) on Chromosorb P
8 m - 20%	Polypropylene Glycol (F & M Scientific) on Chromosorb W
8 m	Glassport M only (Hewlett-Packard), 60-80 Mesh
6 m - 5%	Versamid 900 (Analabs) on Glassport M
5 m - 15%	Silicon Oil SF-96 (General Electric) on Chromosorb P
4 m - 10%	Apiezon N (Shell Oil Company) on Chromosorb P
5 m - 20%	Polyphenyl Ether (Analabs) on Anakrom.

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[a] Chromosorb P, 45-60 Mesh (F & M Scientific).

[b] Chromosorb WAW-DMCS, 45-60 Mesh (F & M Scientific).

[c] Anakrom PA, 50-60 Mesh (Analabs).

Additional discussion of experimental procedures will be presented in the Results and Discussion section since particular experiments were designed to answer specific questions in the various systems studied.

B. Production of ^{11}C

The Iowa State University electron synchrotron produces a bremsstrahlung beam with a maximum energy of 70 MeV. Free atoms of ^{11}C were produced by the nuclear reaction $^{12}C(\gamma,n)^{11}C$ in the sample bulb mounted on a Synthane sample holder and positioned behind a 0.200 inch lead target within the acceleration chamber of the synchrotron. The irradiation periods ranged from 2 to 30 minutes depending upon the beam intensity and the requirements of the experiment. The instrumental techniques employed for these irradiations have been discussed by Hammer and Bureau (112-114). From the photonuclear cross section curve determined by Cook et al. (115) the average carbon recoil energy has been estimated as ~ 0.5 MeV.

The high energy imparted to the carbon atom in the photonuclear process insures the breakage of its chemical bonds and may result in the loss of electrons as well. Evidence has been presented (37, 116) which indicates that neutralization of the carbon ion occurs before it slows to energies of potential chemical interest (< 50 eV). It is generally assumed that the carbon atom is in one of its lower lying electronic states (^3P, ^1D, or ^1S) when it undergoes chemically meaningful reactions but conclusive evidence is lacking. The results of Pohlit et al. (23) suggest that carbon ions are neutralized rapidly even if they enter a hydrocarbon medium at much lower energies.

C. Radiochemical Yield Determination

The separation system is designed to permit the analysis of single samples only. Consequently each sample was independently irradiated at the synchrotron and returned to the laboratory for analysis. The predominant photonuclear reaction produced by the continuous spectrum of high energy photons is $^{12}C(\gamma,n)^{11}C$ but potentially interfering reactions occur particularly in compounds containing oxygen atoms. Two additional reactions which contribute to the observed sample activity are $^{16}O(\gamma,n)^{15}O$ and $^{16}O(\gamma,t)^{13}N$ producing isotopes which are positron emitters, and hence cannot be discriminated from ^{11}C by the analyzer system. Palino used a decay resolution computer program developed by Korthoven and Carlson (117) to evaluate the atomic production rates of ^{15}O and ^{13}N relative to that of ^{11}C and reported ratios of 1.0 and 0.026, respectively. The interference by ^{15}O can be considerably reduced by allowing a cooling period before monitoring the sample activity during which ^{15}O ($t_{1/2}$ = 2.07 min) decays much more rapidly than ^{11}C ($t_{1/2}$ = 20.4 min). For samples irradiated for 4.00 minutes and monitored

23.5 minutes after the end of bombardment Palino (73, pp. 50-52) determined that the ratio of total activity detected to that due to ^{11}C activity ranged from 1.042 for methanol and methyl formate to 1.010 for diethyl ether. Hydrocarbon samples give ratios very close to 1.0 with only minor interference from oxygen in the sample container. The activity induced in an evacuated pyrex sample bulb has been shown to make less than a 1% contribution to the activity monitored 20.0 min after a 4.00 min bombardment. On the basis of these results the induced activity has been assumed to be ^{11}C only with product yields as well as dose and dose rate measurements determined from the observed sample activity monitored by averaging three successive one minute counts beginning 20.0 minutes after termination of bombardment.

An expression relating the activity in a particular peak to the total number of counts observed under that peak has been developed by Wolfgang and Rowland (118) for a flow type proportional counter. Palino (73, p. 40) has modified their expression for application to the flow detection system used in these studies. The yield of any product is equal to the product's activity divided by the total sample activity and may be expressed by the following relationship.

$$\text{Yield (\%)} = \frac{(C - b)\, e^{\lambda_1 t_p}\, (\text{f.r.})}{N_t\, e^{\lambda_1 t_m}\, (\text{c.f.})} \qquad (6)$$

where

λ_1 = decay constant for ^{11}C,

$(C - b)$ = observed counts minus background,

t_p = time after bombardment at which product activity is measured,

$(f.r.)$ = flow rate measured outside heated detector in ml/min,

N_t = total sample activity monitored in standard geometry,

t_m = time after bombardment at which sample activity is monitored,

$(c.f.)$ = system calibration factor relating static and flow sensitivities.

A calibration factor for the determination of absolute yield was carefully determined by Palino (73, pp. 43-46) using a CuO combustion train to quantitatively oxidize irradiated iso-pentane samples for flow counting of $^{11}CO_2$. Six replicate determinations with this system resulted in a calibration factor of 2.775 ± 0.018, i.e., less than 1% uncertainty. This calibration factor is in reasonable agreement with previous calibration results in this laboratory (119, 120) and was ingeniously designed for accurate calibration of the flow system. Results based on this calibration method can be used confidently when interpreting data. Absolute yields of observed products provide information concerning the magnitude and significance of the unobserved or unidentified products which is helpful in evaluating reaction schemes for systems in which a large percentage of the products has been determined. Direct comparisons between systems of yields of particular products are meaningful only if the yields are known on a common basis.

The calibration factor is obviously a function of the individual detection system to which modifications are frequently necessary. To insure accurate and convenient recalibration Palino developed a secondary calibration method which was used periodically throughout this work. The absolute yields and dose dependence of methane, ethane, ethylene, and acetylene for a series of iso-pentane samples were determined in the Palino system of known calibration factor. These yields were used in a modified form of Equation 6 to determine the calibration factor for my system based on each of the four products.

$$(\mathrm{c.f.})_i = \frac{(C - b)\, e^{\lambda_1 t_p}\, (\mathrm{f.r.})}{N_t\, e^{\lambda_1 t_m}\, (\text{known yield})_i} \qquad (7)$$

Using the results of Equation 7 the most precise value for the system calibration factor can be determined by a weighted average of the individual factors.

$$\text{c.f.} = \frac{\sum_{i=1}^{4}\left[\frac{(C - b)\, e^{\lambda_1 t_p}\,(\text{f.r.})}{N_t\, e^{\lambda_1 t_m}}\right]_i (\text{c.f.})_i}{\sum_{i=1}^{4}\left[\frac{(C - b)\, e^{\lambda_1 t_p}\,(\text{f.r.})}{N_t\, e^{\lambda_1 t_m}}\right]_i} \qquad (8)$$

This weights the individual factors by the relative magnitude of the yields of these products. The system calibration factor was determined each week throughout the research period to insure proper operation of the complex analysis system. Using representative data from experiments conducted during spring, 1969, a series of five replicate determinations on five successive weeks gave a calibration factor of 0.350 ± .004. The uncertainty is again on the order of 1%, very similar to the uncertainty in the primary determinations. The use of this secondary calibration method has been invaluable in this work and provides a means of dependable, accurate comparisons between the results obtained and those of Palino (vide infra).

The integrated dose rate at the probe position of the synchrotron was determined by Palino (73, pp. 48-55). The darkening of cobalt glass by exposure to radiation was calibrated using the ^{60}Co source of the I.S.U. Veterinary Medical Research Institute over a range of 8×10^4 to 2×10^6 rads. The objective was to relate the monitored activity of synchrotron irradiated samples to the radiation dose absorbed. Cobalt glass and sample bulbs filled with compounds used in ^{11}C recoil studies were irradiated simultaneously in the synchrotron probe position. Using the calibration curve determined from the γ-ray source the following dose equation can be developed for these studies.

$$\text{Dose (rads)} = \frac{7.70 \times 10^5 \times N_t \times t_b \times 0.1180 \times 10^{17}\, e^{\lambda_1 t_m}}{(1 - e^{-\lambda_1 t_b})\, p_C} \qquad (9)$$

where

t_b = irradiation time in minutes,

0.1180 = proportionality factor relating Palino's monitor to my monitoring system,

p_C = carbon atom density in the sample.

The dose rate is taken as the dose per unit irradiation time. For immediate comparison $\overline{N}_T$ and D_R (vide infra) were calculated for each sample immediately after the analysis. These convenient values for dose and dose rate can then be converted into meaningful units. The definitions are:

$$\overline{N}_T = \frac{.1180 \times N_T\, e^{\lambda_1 t_b} \times t_b \times 10^{17}}{(1 - e^{-\lambda_1 t_b})\, p_C}$$

$$D_R = \frac{\overline{N}_T}{t_b} \times 10$$

For example, the following ranges in dose and dose rate were examined for methanol. The $\overline{N}_T$ values ranged from 1.0 to 20.0 corresponding to doses of 0.0025 to 0.051 eV/molecule, respectively. The D_R values ranged from 2.0 to 12.0 corresponding to dose rates of 0.0005 to 0.0030 eV/molecule·min, respectively. The chemical effects of these dose and dose rate ranges will be discussed in the Results and Discussion section for various compounds. Frequent use of the numerically convenient $\overline{N}_T$ and D_R will be supplemented by reference to meaningful dose and dose rate units.

D. Computer Programs and Analysis

During the course of this research it became apparent that useful computer programs could be written to aid in data analysis, reduction, and interpretation. I have become familiar with the FORTRAN language, practicing by designing programs of particular applicability to these studies.

To insure proper operation of the detection system used two standard samples of ^{22}NaI, one of activity similar to total sample activities and one similar to peak activities, were monitored daily before analyzing samples. A simple program called DSDRIF was written to evaluate the detector system drift by plotting the observed count rates as a function of time to graphically inspect short term fluctuations and long term drift in detector efficiency.

This was particularly important in view of the heated detector tube used in the NaI crystal which is subject to heat damage. Since the single channel analyzer was calibrated to accept pulses between 0.4 and 1.2 MeV minor high voltage or gain shifts would be easily detected by a change in count rate for the ^{22}Na isotope which has a 1.28 MeV γ-ray in addition to positrons in its decay scheme. The decay curve from data obtained during a 900 day period displayed a halflife of 2.20 years with the data points showing no significant system change in efficiency during that time period. The results illustrate the long term stability of the detector system and provide added assurance that results obtained over the experimental period are internally consistent. The iso-pentane calibration samples verify the excellent operational characteristics of this analysis system.

A program was developed by Palino (73, p. 42) which plots the product yields as a function of dose fitting the results to the best least-squares straight line. Modifications of this program were made in this study including adaptation to dose rate analysis. Summaries of the experimental results will be given in appropriate parts of the Results and Discussion section but graphical representations will not be included because of their limited value and voluminous nature. The data plots as well as all the chromatograms in this work will be kept on file in this laboratory.

Another program, SMARYZ, was written to summarize and tabulate the results from the least squares program. Yield values with standard deviations are tabulated for specified doses in the scavenged and unscavenged systems. These results are of value in the development of the carbon monoxide site model which will be discussed later.

A program was written using the I.S.U. Computer Center regression analysis programs to evaluate the dependence of carbon monoxide yield from methanol on dose and dose rate simultaneously. This is equivalent to determining the least-squares best plane through the points of the yield surface above a plot of dose versus dose rate. The results will be discussed in subsequent sections.

The computer program, COFIT, was written to aid in determining molecular site values for the site model used in calculating ^{11}CO yields based on molecular structure. The basic model and the numerical results will be discussed in the Results and Discussion section. The problem is essentially to solve a set of 13 equations in seven unknowns for the best values of the seven parameters. An equation of the following form was written for each of the 13 compounds for which data had been obtained.

$$Y = \frac{X_j}{\sum_{i=1}^{7} n_i X_i} \qquad (10)$$

where

X_i and X_j are values for specific bonds,

n_i is the number of X_i cites in the molecule.

These equations were linearized using the constant and linear terms of a Taylors series expansion about a set of initial values for the parameters. The set of 13 equations of the form

$$Y = Y_o \big|_{X_o} + \sum_{i=1}^{7} \frac{\partial Y}{\partial X_i} \big|_{X_o} (X_i - X_o) \qquad (11)$$

can be written simply as the matrix equation

$$\Delta Y = A \, \Delta X$$

where

$\Delta Y = (Y - Y_o \big|_{X_o})$

$\Delta X = (X_i - X_o)$

A = the matrix of partial derivatives.

For an arbitrary set of initial X_o values the $\Delta X = X_i - X_o$ values can be determined. An improved set, i.e., making ΔY smaller, is generated by $X_o^1 = X_o - \Delta X$. Reiteration in this manner is repeated until $\Sigma (\Delta Y)^2$ is minimized. The final X_o^1 values determined from this procedure are the best values for the molecular site values resulting in the best agreement between observed and calculated yields of ^{11}CO from the alcohols and ethers studied. The iterative procedure in this program not only leads to a minimum value of $\Sigma\ (\Delta Y)^2$, i.e., converges, but results in the same normalized set of site values from a wide range of nonzero initial values suggesting the uniqueness of the best set, i.e., no false minima.

The elementary usage of FORTRAN computer programing involved in this work has been a valuable aid in data reduction and interpretation. Continued and extended computer work is highly recommended for future hot atom research studies.

III. RESULTS AND DISCUSSION

A. Reactions of ^{11}C in Selected Aromatic Compounds

Investigations of carbon reactions in benzene (121-123) have suggested that aromatic compounds present some reactions which are quite different from those observed with other hydrocarbons. In addition to the common C-H bond insertion and hydrogen abstraction reactions, reactions involving the aromatic ring directly are the subject of this section. The intent was to provide information to compare analogous reaction pathways in the three systems, benzene, toluene, and p-xylene as an aid to a better understanding of the reactions which occur in aromatic compounds.

The product yield results for the aromatic compounds are presented in Tables 3 through 5. The yield values listed are the absolute percentages of the total ^{11}C produced in the system as determined by the method discussed in the experimental section. Each system was studied over a range of total dose (0.015-0.090 eV/molecule) and each product yield was examined for dose dependence using the least squares computer program. In none of the observed products was the dose dependence significant when compared with its uncertainty due to experimental scatter. This is in direct contrast with the results in the other systems to be discussed later. Therefore the reported yield values are the averages and standard deviations over the entire

Table 3. Product yields from benzene

Product	Unscavenged	1 x 10^{-3} DPPH
methane	.18 ± .03	.43 ± .06
acetylene	4.68 ± .14	4.59 ± .24
allene	.14 ± .04	.13 ± .03
methylacetylene	.16 ± .05	.14 ± .05
(vinylacetylene)[a]	.55 ± .05	.62 ± .10
(diacetylene)	1.58 ± .30	1.97 ± .16
benzene	3.54 ± .22	2.85 ± .10
B-1	.21 ± .04	.35 ± .07
B-2	.28 ± .03	.26 ± .14
toluene	2.64 ± .14	2.72 ± .15
cycloheptatriene	3.19 ± .33	2.13 ± .21
p-xylene	.36 ± .06	.52 ± .14
m-xylene	.25 ± .03	.29 ± .04
o-xylene	.15 ± .04	.20 ± .02
ethylbenzene	.22 ± .05	.24 ± .08
styrene	.53 ± .13	.36 ± .09
phenylacetylene	1.90 ± .26	2.88 ± .15
B-3	.30 ± .07	.29 ± .06
Total identified	20.86	20.97

[a] Products in parentheses are tentatively identified by retention time.

Table 4. Product yields from toluene

Product	Unscavenged	1×10^{-3} DPPH
methane	.49 ± .03	.51 ± .02
ethylene	.65 ± .06	.64 ± .06
acetylene	5.41 ± .24	5.32 ± .20
allene	.15 ± .04	.12 ± .02
methylacetylene	.55 ± .07	.50 ± .05
(vinylacetylene)[a]	.46 ± .07	.61 ± .04
(valylene)	.08 ± .02	.09 ± .02
(1-penten-3-yne)	.10 ± .03	.11 ± .03
(diacetylene)	.67 ± .13	1.25 ± .06
benzene	.59 ± .13	.48 ± .06
toluene	2.70 ± .16	2.31 ± .12
(3-methylcycloheptatriene)	.11 ± .03	.17 ± .02
(2-methylcycloheptatriene)	.14 ± .02	.22 ± .05
(1-methylcycloheptatriene)	.29 ± .06	.34 ± .06
p-xylene	.77 ± .03	.76 ± .05
m-xylene	1.05 ± .04	.94 ± .05
o-xylene	1.15 ± .14	.99 ± .09
ethylbenzene	3.65 ± .15	3.37 ± .21
styrene	3.77 ± .18	4.24 ± .16

---

[a] Products in parentheses are tentatively identified by retention time.

Table 4. (Continued)

Product	Unscavenged	1 x 10^{-3} DPPH
phenylacetylene	.94 ± .10	1.24 ± .08
1,2,4-trimethylbenzene	.16 ± .04	.13 ± .04
1,3,5-trimethylbenzene	.09 ± .02	.16 ± .02
(ethyltoluenes)	.20 ± .10	.30 ± .04
(methylstyrenes)	.50 ± .06	.30 ± .03
(methylphenylacetylenes)	1.10 ± .10	1.59 ± .11
Total identified	25.77	26.69

Table 5. Product yields from para-xylene

Product	Unscavenged	1 x 10^{-3} DPPH
methane	.88 ± .06	1.04 ± .08
ethylene	1.27 ± .14	1.16 ± .09
acetylene	5.95 ± .28	5.68 ± .21
allene	.29 ± .08	.22 ± .02
methylacetylene	.86 ± .20	.69 ± .05
(vinylacetylene)[a]	.50 ± .08	.53 ± .07
(valylene)	.14 ± .02	.16 ± .02
(1-penten-3-yne)	.20 ± .03	.19 ± .02
(diacetylene)	.65 ± .05	.82 ± .06
(1,3-heptadiene-5-yne)	.20 ± .03	.22 ± .04
toluene	1.11 ± .17	.84 ± .07
p-xylene	2.40 ± .18	2.06 ± .10
(1-4- and 2,5-dimethylcyclo-heptatriene)	.97 ± .18	.95 ± .13
o-xylene	.63 ± .18	.46 ± .09
styrene	1.01 ± .13	1.28 ± .14
phenylacetylene	.57 ± .07	.68 ± .10
1,2,4-trimethylbenzene	2.13 ± .24	2.36 ± .22
p-ethyltoluene	5.09 ± .21	5.23 ± .35

---

[a] Products in parentheses are tentatively identified by retention time.

Table 5. (Continued)

Product	Unscavenged	1×10^{-3} DPPH
p-methylstyrene	7.02 ± .24	7.91 ± .19
(p-methylphenylacetylene)	1.18 ± .11	1.67 ± .19
(2,5-dimethylstyrene)	.39 ± .10	.47 ± .11
(2,5-dimethylphenylacetylene)	.71 ± .07	1.16 ± .16
Total identified	34.15	35.78

dose range studied. The number of data points used in this analysis was from 10 to 20 for the various products in the three systems.

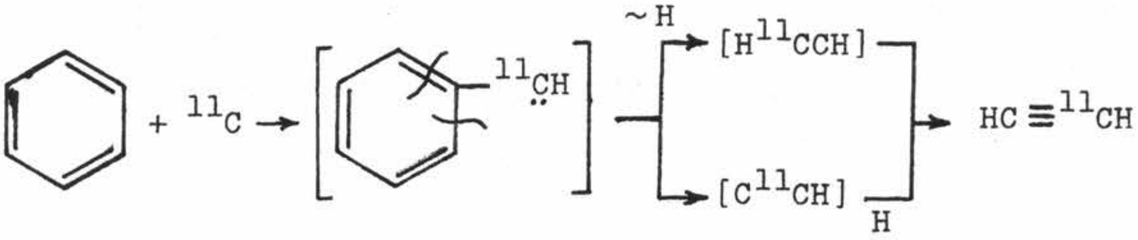
The obvious difficulties of a mechanistic treatment of these systems include the large number of products, the small percentage of the total activity identified, and the extreme fragmentations and rearrangements required for the production of some of the products. Several reaction intermediates have been proposed in previous discussions of the benzene system. Suryanarayana and Wolf (46) have suggested a seven-member ring as an insertion intermediate with alternative stabilization and rearrangement routes. Rose _et_ _al_. (74) proposed several adducts with π-bonded configurations and discussed the energetics of fragmentation of these intermediates. The results here are shown to be consistent with these proposals and a seven-member ring insertion intermediate will be used to lead to a number of products by fragmentation, stabilization, or by undergoing bimolecular reaction. The validity of proposed intermediates in this work can be evaluated on the basis of the final product yields supplemented by degradation studies conducted in other laboratories. The lack of detailed information about intermediates in these systems was discussed in a previous section.

The low yield of methane from benzene is consistent with trends observed in paraffins and olefins in which the methane yield is a function of the availability of hydrogen. Since methane is the final product of a series of abstraction reactions its yield in any system reflects the overall reactivity of carbon in that system in which various other reactions compete for the carbon atom as it slows to thermal energies. Thus benzene appears to be the most reactive system toward recoil ^{11}C with more than 99.8% of the carbon atoms reacting by reactions other than methane formation. In the systems with methyl groups the increased hydrogen availability results in larger yields of methane consistent with the successive hydrogen abstraction route and indicating competition between this and other reactions in toluene and p-xylene.

In the presence of radical scavenger the methane yield increases in all three systems. This is interpreted as a marked decrease in the reactivity of the system by reduction of the concentration of radiation produced radicals. In the case of benzene a large percentage of the ^{11}C will be shown to reside in polymeric materials the production of which appears to involve radiation species. If these polymerization reactions are attenuated the carbon atom finds itself in a less reactive medium making methane formation a relatively more important reaction.

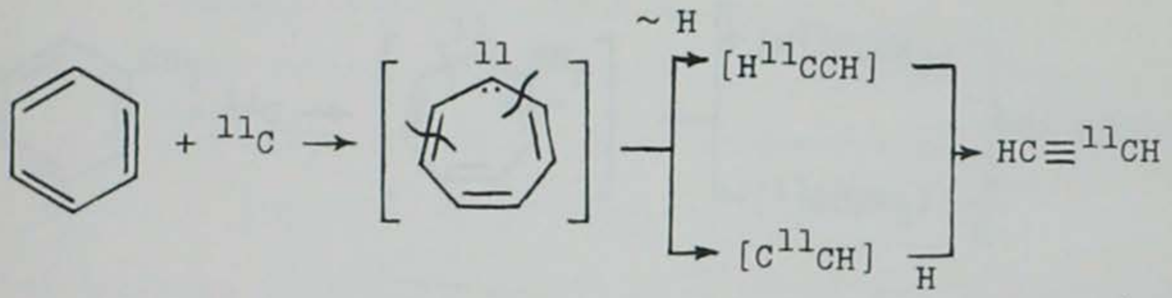
Ethylene was identified in the toluene and p-xylene systems but not in benzene indicating that it is produced by reactions at the methyl sites as has been well studied by other workers in alkane systems. The ethylene yield doubles with the presence of the second methyl group in p-xylene which is consistent with the statistical development of Clark and Voigt (55).

The formation of acetylene provides the first example of direct involvement of the aromatic ring. One reaction route for the production of acetylene from benzene is ^{11}C atom insertion into a C-H bond followed by rupture of the two adjacent ring bonds (β to the ^{11}C) to free the labeled C_2 moiety, with the additional hydrogen atom obtained by intramolecular hydrogen transfer or by hydrogen pickup from the medium after separation.



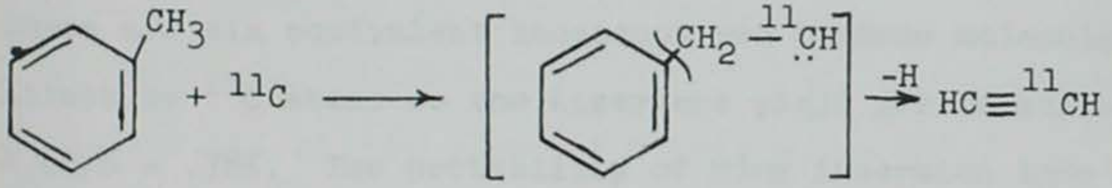
(12)

A second type of mechanism is ^{11}C atom insertion into the ring followed by rupture of α and β bonds again with either a hydrogen shift or subsequent hydrogen pickup.



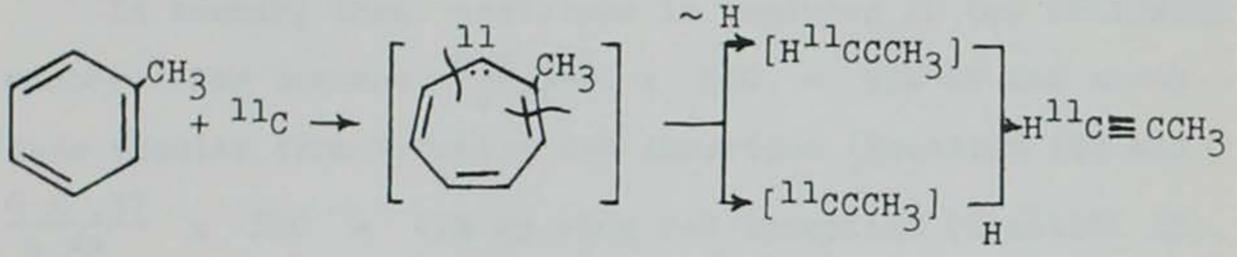
(13)

If the compound contains a methyl group additional pathways are available including insertion into a side-chain C-H bond.



(14)

In the methyl derivatives reactions similar to Equation 13 will lead to methylacetylene, which is observed in very small yield in benzene and in considerably larger yield in toluene and p-xylene. This increase in yield is most probably due to ^{11}C atom insertion into a ring bond adjacent to the side chain. This ring insertion hypothesis is supported by the fact that no three carbon product containing the methyl group can result from ring C-H bond insertion since two ring-carbon atoms would be present between the insertion site and the methyl group.



(15)

The relative production of acetylene by Equations 12, 13, and 14 can be estimated as follows. The data on unscavenged systems are used and those from the scavenged systems give similar results. For both Reactions 12 and 13 there are six equivalent locations per benzene molecule for attack by ^{11}C atoms so the acetylene yield per location is 4.68/6 = .78%. The probability of ring insertion into toluene to form methylacetylene can be considered to be the difference in the yield of this product in toluene and benzene (.39%) or half this difference for p-xylene (.35%). The average of these values (.37%) can be used as the yield per location for Reaction 13 in benzene if it is assumed that this process is not changed by the presence of the methyl groups. The yield from Reaction 12 per site is then .78 - .37 = .41%. The acetylene yield by side-chain C-H bond insertion can be estimated by subtracting the expected yields for five locations around the ring (5 x .78 = 3.90%) from the total acetylene yield from toluene (5.41 - 3.90 = 1.51%) which ascribes 0.50% per C-H bond. A similar calculation for p-xylene gives 0.47% as the yield per C-H bond.

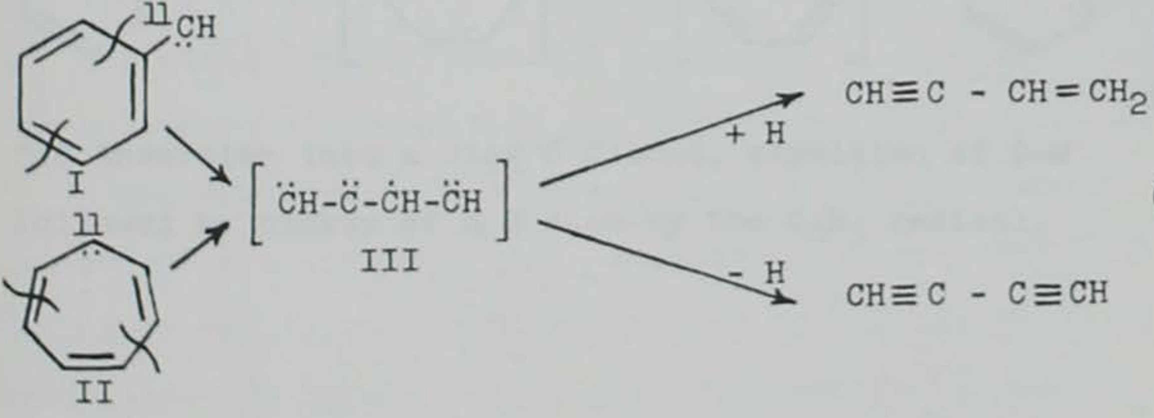
In summary then, acetylene is produced in the following manner. For benzene, $\frac{6 \times .41}{4.68} \times 100 = 53\%$ of the acetylene results from aromatic C-H insertion (Reaction 12) and $\frac{6 \times .37}{4.68} \times 100 = 47\%$ by ring C-C insertion (Reaction 13). For toluene, (5 x .41 x 100)/5.41 = 38% of the acetylene results from Reaction 12, (5 x .37 x 100)/5.41 = 34% from Reaction 13, and (3 x .50 x 100)/5.41 = 28% by methyl C-H insertion (Reaction 14). By this scheme the acetylene production from p-xylene may be ascribed 27% to Reaction 13, 24% to Reaction 14, and 49% to Reaction 15.

Additional discussion of these acetylene producing reactions can be made from the experimental results of Ache _et_ _al_. (69). Using mixtures of perdeuterated as well as selectively deuterated compounds they showed that C atom insertion in these types of reactions is more important for the formation of acetylene than insertion of methyne into the ring followed by similar rupture processes. I will show that the reactions proposed here account for their results without invoking any contribution from methyne reactions. They observe 8.8% of the acetylene to be $HC{\equiv}CD$ from a 1:1 mixture of C_6H_6 and C_6D_6 whereas CH and CD insertion would result in 50% of the mixed product. The low percentage of mixed acetylene shows that the hydrogen pickup alternatives in Equations 12 and 13 are of minor importance since they would also lead to 50% CD≡CH in the mixed system.

The existence of these hydrogen pickup steps is supported by the results from a 1:1 mixture of C_6H_6 and CD_4 (69). The acetylene yield is analyzed to be 22.4% C_2H_2, 5.0% C_2HD, and 72.6% C_2D_2. The total acetylene yield is much higher for methane than for benzene accounting for the large C_2D_2 yield but the 5% yield of mixed acetylene can be used to estimate the importance of hydrogen pickup from the medium. All of the C_2H_2 is produced from the benzene, and since acetylene formation from methane is even more specifically intramolecular (less than 2% mixed acetylene from CH_4:CD_4), the D atom pickup by a C_2H fragment produces $[5.0 - (< 2.0 \times .73)]/27.4$ to $25.9 = 13$ to 19% of the acetylene from benzene. Since D atom pickup is much more probable than H atom pickup in this medium, one concludes that 13 to 19% of the acetylene formed in Reactions 12 and 13 occur by hydrogen pickup. Whether hydrogen shifting is more favorable in one case than the other cannot be determined from the available data. This numerical analysis would predict the yield of mixed acetylene at 6.5 to 9.5% which is in good, but possibly fortuitous, agreement with the experimental 8.8% in view of the use of two distinct experimental systems and the accumulative approximations in the treatment.

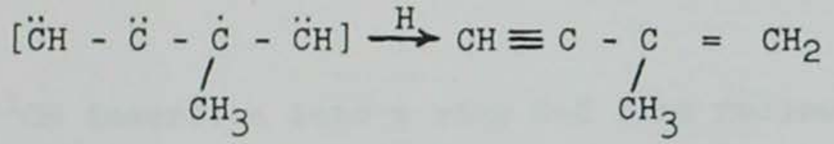
One final comparison can be made using Ache's acetylene data from $C_6H_5CD_3$. The C_2D_2/C_2H_2 ratio is 0.373 indicating that reaction with the ring is more productive than with the methyl group. Making a similar calculation with the results presented here gives the methyl group to ring formed acetylene ratio as $(3 \times .50)/(5 \times .78) = 0.385$ which agrees better than might be expected. I believe that the reactions presented here, with their relative contributions to the acetylene yields from aromatic compounds, are a valuable result of these studies and a good example of the reactions of ^{11}C with the aromatic ring which have no analogies in the nonaromatic hydrocarbons.

Other highly unsaturated products from similar reactions are observed in small to appreciable yields. Intermediate I from C-H insertion or II from insertion into a ring C-C bond (Equation 16) can fragment to give vinylacetylene or diacetylene, both of which were tentatively identified on the basis of retention times.



(16)

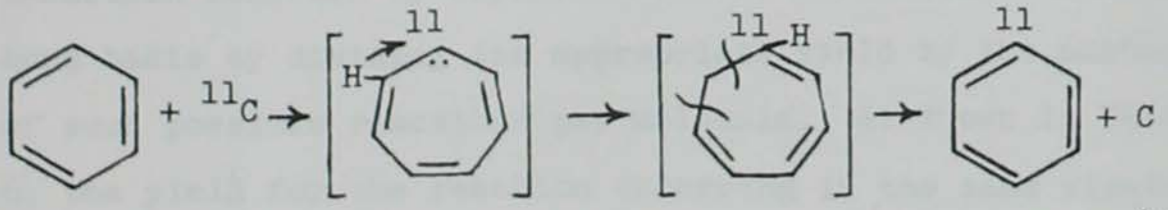
The presence of a methyl group on the ring could change intermediate III to a methyl derivative (Equation 17) which on adding a hydrogen atom would lead to a pentenyne such as valylene or its straight chain isomer.



$$[\ddot{C}H - \ddot{C} - \underset{CH_3}{\dot{C}} - \ddot{C}H] \xrightarrow{H} CH \equiv C - \underset{CH_3}{C} = CH_2 \qquad (17)$$

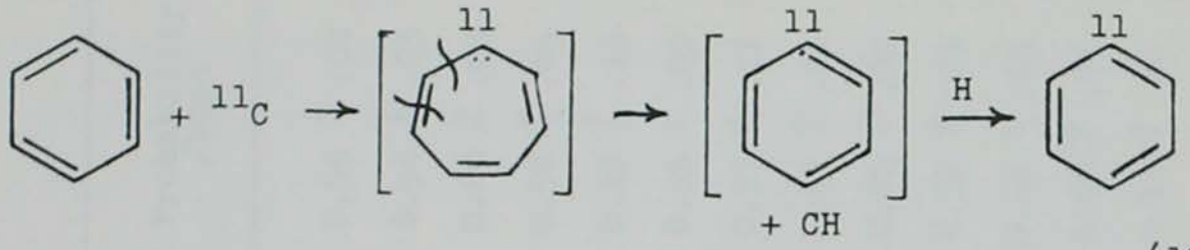
The other, less well-identified fragmentation products are expected to have similar formation paths.

The relatively high yield of labeled parent compound in aromatic systems is entirely unexpected by extrapolation from other hydrocarbon systems and is an important example of ring reactions. Plausible reaction routes include ${}^{11}C$ insertion into a ring C-C bond followed by a hydrogen shift and expulsion of a carbon atom to return to a six-membered ring,



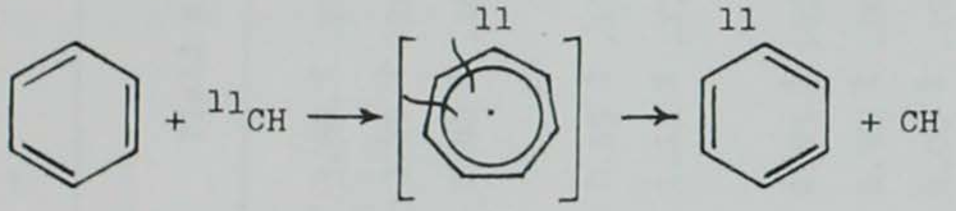
(18)

${}^{11}C$ insertion into a ring C-C bond, expulsion of C-H followed by pickup of a H atom by the C_6H_5 radical,



(19)

and ^{11}CH insertion into a ring C-C bond followed by expulsion of a different CH entity.



(20)

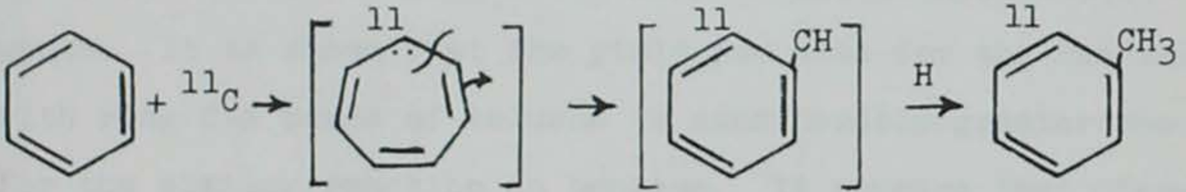
In the methyl derivatives expulsion of a carbon atom with an attached methyl group will produce the simpler homolog, benzene from toluene and toluene from p-xylene, which leads to an interesting comparison. A probability of insertion followed by expulsion can be calculated on a per bond basis by dividing the appropriate yield by the number of such possible reactions per molecule. As shown in Table 6, the yield for the reaction occurring is the same within experimental error whether the leaving group is CH or CCH_3.

The addition of a ring methyl group to the parent compound occurs in all three aromatic systems. The most probable mechanism for this reaction is the insertion of methylene-^{11}C into a ring C-H bond. However, degradation

Table 6. Probability of expulsion reaction

Reactant	Product	Conditions	Yield %	No/mol	Probability /bond
bz	bz	unscav.	3.54 ± .22	6	0.59 ± .04
tol	tol	unscav.	2.70 ± .16	5	0.54 ± .03
xyl	xyl	unscav.	2.40 ± .18	4	0.60 ± .05
Av					0.58 ± .04
tol	bz	unscav.	0.59 ± .13	1	0.59 ± .13
xyl	tol	unscav.	1.11 ± .17	2	0.55 ± .09
Av					0.57 ± .11
bz	bz	scav.	2.85 ± .10	6	0.47 ± .02
tol	tol	scav.	2.31 ± .12	5	0.46 ± .02
xyl	xyl	scav.	2.06 ± .10	4	0.52 ± .03
Av					0.48 ± .03
tol	bz	scav.	0.48 ± .06	1	0.48 ± .06
xyl	tol	scav.	0.84 ± .07	2	0.42 ± .04
Av					0.45 ± .05

studies (23,100,124) on toluene-^{14}C produced by the action of energetic ^{14}C atoms on benzene have shown that 12-14% of the label is in the ring, not exclusively in the methyl group. A different mechanism is required for the explanation of this part of the toluene yield. A possibility is shown in Equation 21 in which ring insertion by a carbon atom is followed by collapse of the seven-member intermediate with the ring-excluded carbon remaining attached to the ring by one bond and subsequent hydrogen pickup to form toluene.



(21)

This mechanism was suggested (75) as a natural extension of the insertion-expulsion reactions proposed for parent production. Very recently supporting evidence has been presented by Lemmon <u>et al</u>. (125). They find a marked decrease in toluene yield in their experiments as the ^{14}C ion energy is decreased from 100 eV to 5 eV suggesting a decrease in the methylene insertion reaction due to insufficient energy to produce the required methylene-^{14}C reactant. Concurrent degradation studies reveal that the percentage of ring activity increases as would be expected if the C atom were producing a larger fraction of the toluene at lower energies by the ring insertion mechanism proposed here. This emphasizes the similarities between our ^{11}C recoil work and the accelerated ^{14}C ion studies.

Since the insertion-expulsion mechanism accounts for only a small part of the n + 1 product yield for high energy recoil studies, the yields for these products can be compared on the basis of the predominant methylene insertion into ring C-H bonds. Such a comparison is shown in Table 7 along with similar data on the products of methylene insertion into a C-H bond of the methyl substituents. It is shown that the yield per site for the reaction with ring C-H bonds of toluene is considerably greater than for the similar reaction in benzene. It appears that there is a strong preference for para attack, with ortho and meta following in that order but not widely different. The per site yield for this reaction occurring in p-xylene is similar to that for the ortho and meta positions in toluene, considerably larger than for benzene sites.

An interesting analysis of the apparent steric and electronic effects of methyl substituents on this reaction can be made using the results of Table 7. If it is assumed that the electronic effect on the ortho and para positions is the same, both effects can be evaluated by comparing the results of toluene and benzene as follows. The yield at the para position is the benzene site value plus the

Table 7. Methylene additions to aromatic hydrocarbons

Reactant	Product	Conditions	Yield %	Bonds/mol	Probability /C-H bond
bz	tol	unscav.	2.70 ± .16	6	0.45 ± .03
tol	p-xyl	unscav.	0.77 ± .03	1	0.77 ± .03
tol	m-xyl	unscav.	1.05 ± .04	2	0.52 ± .02
tol	o-xyl	unscav.	1.15 ± .14	2	0.57 ± .07
tol	Σxyl's	unscav.	2.97 ± .15	5	0.59 ± .03
pxyl	1,2,4 tmb	unscav.	2.13 ± .24	4	0.53 ± .06
tol	et bz	unscav.	3.65 ± .15	3	1.22 ± .05
pxyl	p-et tol	unscav.	5.09 ± .21	6	0.85 ± .04
bz	tol	scav.	2.31 ± .12	6	0.38 ± .02
tol	p-xyl	scav.	0.76 ± .05	1	0.76 ± .05
tol	m-xyl	scav.	0.94 ± .05	2	0.47 ± .03
tol	o-xyl	scav.	0.99 ± .09	2	0.50 ± .05
tol	Σxyl's	scav.	2.69 ± .11	5	0.54 ± .02

Table 7. (Continued)

Reactant	Product	Conditions	Yield %	Bonds/mol	Probability /C-H bond
pxyl	1,2,4 tmb	scav.	2.36 ± .22	4	0.59 ± .06
tol	et bz	scav.	3.37 ± .21	3	1.12 ± .07
pxyl	p-et tol	scav.	5.23 ± .35	6	0.87 ± .06

electronic enhancement (E) from one methyl group, .77 = .45 + E, so E = + .32. The yield at the ortho position is affected by steric blocking (S) by the methyl group hence .57 = .45 + E + S, so S = .45 + .32 - .57 = - .20. The yield at the meta position is increased much less by the electronic effect, .52 - .45 = .07, which is what is expected for an electron donating substituent.

Results for p-xylene where each of the four ring C-H bonds is meta to one methyl group, ortho to the other, and is sterically shielded by one methyl group give the following calculated value. The yield of 1,2,4-trimethylbenzene per site is the sum of the benzene value, the meta electronic effect, the ortho electronic effect, and the steric blocking, .45 + .07 + .32 - .20 = .64, which is slightly above the experimental value .53 ± .06. This suggests, as might be expected, that the electronic effects of the two methyl groups are somewhat less than additive, resulting in a high yield estimate. This analysis is based on data from so few compounds that it is at best a hypothesis and must be tested by additional results if the conclusions are to be meaningful. Further discussion of the magnitude of the methyl effect is not warranted.

The idea of directed attack by methylene on methyl substituted benzene is surprising since methylene is known to be a nondiscriminating reagent and one would expect that energetic methylene would show even less discrimination. Very little has been published on the reactions of methylene with substituted benzenes. Terao and Shida (126) studied the photolysis of ketene in toluene in the gas phase at a few centimeters pressure. Their results are quite different from those of the present experiments, but the conditions were also quite different. The methylene which appeared in addition products was distributed as follows: 40% m-xylene, 25% p-xylene, 25% ethylbenzene, and ~ 0% o-xylene. The absence of o-xylene was attributed to steric hindrance.

Meerwein *et al*. (127) reported that in the photolysis of diazomethane in anisole nearly equal amounts of the o-, m-, and p-methoxytoluenes were produced, which would indicate an approximately twofold preference for para insertion. The only agreement among the results of these very different experiments is that para insertion appears to be favored above the expected value of 20% of the total yield for the three isomers.

Methylene additions to the side chain forming ethylbenzene from toluene and p-ethyltoluene from p-xylene are also observed in good yield. The yields per C-H bond are 1.22 in toluene and 0.85 in p-xylene which are significantly different. The only simple explanation is that since methylene-^{11}C is not a very abundant species in these reactive aromatic compounds the lower per bond yield in p-xylene reflects an inadequate supply of methylene to produce the high yield expected with the two methyl groups. One must realize that 7.3% of all the ^{11}C atoms produced in the system would be required in the methylene form for this reaction alone and that this reaction must compete with others for the limited supply of methylene-^{11}C.

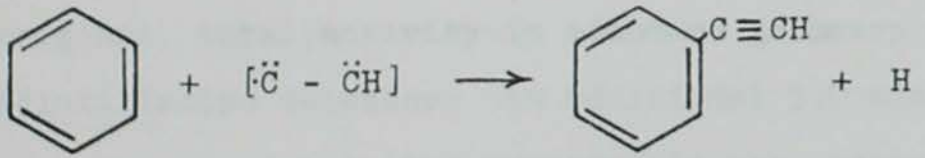
The major reaction by which styrene is produced from toluene and p-methylstyrene from p-xylene is most likely ^{11}C atom insertion into a C-H bond followed by stabilization as the olefin by intermolecular hydrogen transfer. This is a well documented reaction observed in many aliphatic systems. On a per bond basis the yields from this reaction are the same for toluene (1.25) and p-xylene (1.17) reflecting an abundant reactant which is capable of producing high yields of products without deviation due to competitive reactions.

The formation of phenylacetylene from toluene (and of p-methylphenylacetylene from p-xylene) by ^{11}C atom insertion into a methyl C-H bond requires that two hydrogen atoms be lost. The comparable aliphatic reaction

$$R - CH_3 + {}^{11}C \rightarrow [RCH_2 - {}^{11}C - H] \rightarrow RC{\equiv}{}^{11}CH + 2\ H \qquad (22)$$

has only been reported (49, 53) previously in the case of methane (R = H) in the vapor phase. Special experiments were conducted in which yields of 2.3% hexyne-1 from n-pentane and 2.0% heptyne-1 from n-hexane were determined.

These products lend some support to the proposed double hydrogen loss for the aromatic compounds toluene and p-xylene where the yields are 0.94 and 1.18%. A numerical comparison is difficult in view of competing reactions. Increased ability to transfer excess excitation energy to other parts of the molecular intermediate would tend to reduce loss of a two carbon fragment but would have the same effect on hydrogen atom loss. The overall effect as the R group is varied is not apparent. Comparisons between the aliphatic and aromatic cases are further complicated by an additional pathway, replacement of a ring substituent by a C_2 fragment as shown in Equation 23. Phenylacetylene could be produced from toluene by replacement of the methyl group in this manner.



(23)

The addition of labeled C_2H_x fragments to the aromatic ring results in a group of products which are observed in each of the three compounds studied. The only one of these which has been reported previously is phenylacetylene from benzene. Pohlit et al. (23) reported studies on phenylacetylene produced by accelerated ^{14}C ions with solid benzene finding ~ 96% of the label in the side chain suggesting attachment of a labeled C_2 fragment to the ring. The formation of labeled C_2H fragments is shown in Equations 12 and 13 and less unsaturated fragments could result from hydrogen pickup or abstraction. These C_2H_x reactions on the ring apparently account for styrene and ethylbenzene from benzene and analogous products in the other systems.

Additional experiments were designed to determine the fate of the unidentified 80% of the ^{11}C activity since only ~ 20% of the total activity has been adequately identified. To estimate the amount of ^{11}C-containing "polymer" formed, irradiated samples in their 0.2 ml bulbs were heated to various temperatures in a constant temperature bath after breaking the stem of the bulb and held for 5.0 min. The sample bulbs were removed from the bath and the residual activity was counted and compared with the original, total activity in standard geometry above the scintillation detector. An additional 5.0 min heat treatment at any step in the process did not change the residual activity at that temperature.

In a second experiment the bulbs were broken in the chromatograph in the usual manner and passed through a short column length (2.5 x 0.5 cm) packed with polyphenyl ether on Chromosorb P attached immediately downstream from the breaker. Empty tubing carried the more volatile portion to the gas-flow counter for the measurement of the fraction removed in each temperature interval. The 2.5 cm section was removed and counted.

The results of these experiments are summarized in Table 8. More than 60% of the total carbon activity is retained on the 2.5 cm length of column at 225° and is thus composed of compounds containing three or more benzene rings. In the distillation experiment 32% remained in the uncrushed bulb at 225° and was contained in a visible, viscous residue. The difference, ~ 28%, is attributed to compounds with boiling points considerably above 225° which decompose at this temperature or are carried by the benzene vapor in the distillation experiment but are trapped and protected from decomposition by the column material. Two-ring compounds such as biphenyl, diphenylmethane, fluorene, and phenylcycloheptatriene account for ~ 16%, but in this work they were not resolved sufficiently in the heated counting cell for the determination of accurate yield values. The maze of possible products and reactions involved in polymerization is beyond the scope of the work presented in this thesis and would require the development of techniques different from those used in this study.

The study of the ^{11}C reactions in the aromatic compounds was conducted to obtain accurate yields of as many labeled products as possible. It was hoped that these yields would be of value in evaluating proposed reaction

Table 8. Results of distillation experiments

A. Distillation from sample bulb[a]

T° C	Activity remaining %	Activity removed in temp. increment, %
25	94.7	5.3
100	60	35.
125	53	7.
150	39	14.
175	36	3.
200	33	3.
225	32	1.

B. Elution from 2.5 cm column with flow counting[b]

T° C	Activity in short column, %	Activity removed in temp. interval, %
25	not determined	5.3
25-100	78.0	15.6
100-225	61.2	16.5

---

[a] Average values for five determinations.

[b] A column section (2.5 x 0.5 cm) packed with polyphenyl ether on Chromosorb P was attached immediately downstream from sample breaker. This section was removed and its activity determined in a standard geometry.

Table 8. (Continued)

C. Summary

	Approximate % of total
Products analyzed and identified	20.8
Two-ring compounds[c]	16.
Others distilling to 225° (but not eluted from column in B)	28.
Residual activity at 225°	35.

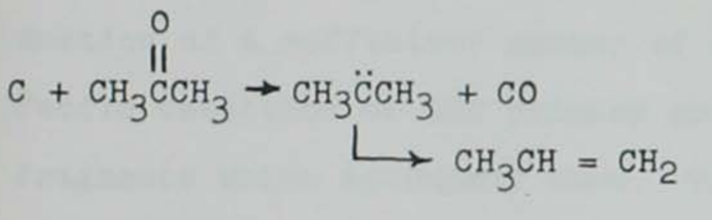
[c] Carrier samples of these compounds were separated by mass detection but poor resolution of the corresponding activity prohibited detailed analysis.

mechanisms and in suggesting additional mechanisms. The extent to which these purposes were fulfilled has been presented.

B. Structural Dependence of Carbon Monoxide Yields

The study of the reactions of atomic carbon with oxygen containing molecules presents an interesting comparison and extension of the reactions observed in hydrocarbons. In general, nuclear recoil techniques prohibit the presence of elements other than carbon and hydrogen in view of the production of isotopes which would interfere with activity measurements and complicate the chemical situation by their own recoil chemistry. It has been shown in a previous section that oxygen containing molecules may be subjected to ^{11}C recoil studies without significant interference principally due to the relatively short half-life of the oxygen isotope produced in the synchrotron irradiation. The presence of an oxygen atom in a small molecule substantially alters its electronic structure compared with a similar hydrocarbon presenting a severely modified substrate for attack by the electrophilic carbon atom. Bonds with high charge density and nonbonding electron pairs would be very favorable attack sites and would be expected to lead to a variety of high yield products.

Palino (73) has reported preliminary results for several alcohols and ethers. A major reaction product in all cases was carbon monoxide presumably produced by a deoxygenation process. At approximately the same time Skell et al. (79) reported deoxygenation in several ketones and ethers, but at that time observed no carbon monoxide formation from simple alcohols and water. The process is illustrated for deoxygenation of acetone.



$$\begin{array}{l} C + CH_3\overset{\overset{O}{\|}}{C}CH_3 \rightarrow CH_3\ddot{C}CH_3 + CO \\ \qquad\qquad\qquad\quad \hookrightarrow CH_3CH = CH_2 \end{array} \qquad (24)$$

Approximately equal amounts of carbon monoxide and alkene products are produced and experiments using vaporization of ^{14}C-enriched graphite demonstrate that only the CO contains the label. More recently Skell and Harris have reported (80) substantial yields of carbon monoxide from simple alcohols (vide infra), a direct contradiction of his earlier results with no apparent explanation.

The Skell experiments (84) involve the generation of low energy carbon atoms by vaporization techniques and subsequent reaction with organic compounds on the liquid nitrogen cooled surface of the reaction chamber. Results of reactions of carbon with alkanes and alkenes by this technique differ widely from recoil carbon results and suggest that major differences exist between these methods. The participation of the cold surface and surface activated C_N species as carbon atom donors, and the nature of the carbon species generated by the vaporization process are suggested, in addition to the lack of kinetic energy, as possible explanations for this great disparity. For this reason the deoxygenation results of Skell will be used with caution for comparison with the results reported here. A major advantage of the vaporization technique is the production of a sufficient number of carbon atoms to permit facile detection of the primary products and the molecular fragments which accompany them. The use of ^{14}C, in either the carbon source or specifically labeled organic compounds, and deuterium labeling in this system where mass balance is possible can provide more detailed information concerning reaction mechanisms than is possible in recoil systems. It is unfortunate that the same reactions of carbon atoms are generally not observed.

The yields of C_1 and C_2 products from some alcohols and ethers are presented in Table 9. All the yields are precisely known as evidenced by the magnitude of error limits. These compounds were selected principally to extend the carbon monoxide data to compounds with more widely differing structure than previously determined by Palino (73). The magnitude and dose dependence of the hydrocarbon product yields were thoroughly discussed in that work and no new interpretations have resulted from the additional data. The hydrocarbon products result principally from

Table 9. Yields of C_1 and C_2 products from alcohols and ethers

System product	Unscavenged	
	-[a]	-[b]
n-butanol		
carbon monoxide	9.26 ± .36	8.26 ± .60
methane	4.98 ± .23	5.40 ± .17
ethane	.48 ± .04	.45 ± .05
ethylene	4.28 ± .19	4.38 ± .23
acetylene	11.10 ± .70	9.56 ± .39
iso-butanol		
carbon monoxide	10.29 ± .05	10.34 ± .13
methane	5.02 ± .09	5.29 ± .09
ethane	.99 ± .15	.87 ± .17
ethylene	7.47 ± .16	7.00 ± .12
acetylene	14.62 ± .50	12.01 ± .79
sec-butanol		
carbon monoxide	11.78 ± .23	11.75 ± .21
methane	4.68 ± .53	4.82 ± .31
ethane	.91 ± .09	.95 ± .10

---

[a] Total dose = 0.010 eV/molecule.

[b] Total dose = 0.050 eV/molecule.

1×10^{-3} I_2		5×10^{-3} I_2	
a	b	a	b
9.87 ± .19	9.83 ± .16	10.28 ± .34	10.34 ± .32
3.26 ± .10	3.12 ± .10	2.76 ± .08	2.76 ± .06
.41 ± .07	.43 ± .06	.39 ± .03	.30 ± .03
4.06 ± .24	3.90 ± .18	3.58 ± .12	3.63 ± .33
11.86 ± .37	11.55 ± .38	11.93 ± .19	11.96 ± .14
10.09 ± .20	10.67 ± .22	10.46 ± .14	10.93 ± .17
2.91 ± .15	3.12 ± .21	2.55 ± .06	2.82 ± .17
.50 ± .05	.71 ± .06	.58 ± .09	1.18 ± .12
6.50 ± .31	7.19 ± .47	5.51 ± .33	6.43 ± .33
13.48 ± .57	14.61 ± .18	14.02 ± .45	14.29 ± .36
12.50 ± .19	12.27 ± .19	13.52 ± .26	12.60 ± .22
2.77 ± .14	2.93 ± .08	2.56 ± .13	2.53 ± .01
.74 ± .07	.69 ± .11	.57 ± .02	.53 ± .02

Table 9. (Continued)

System product	Unscavenged	
	a	*b*
sec-butanol cont.		
ethylene	6.32 ± .12	6.44 ± .14
acetylene	14.16 ± .54	10.44 ± .67
tert-butanol		
carbon monoxide	13.24 ± .40	12.15 ± .51
methane	2.73 ± .06	2.87 ± .17
ethane	1.70 ± .22	1.68 ± .15
ethylene	13.36 ± .47	12.49 ± .64
acetylene	20.74 ± .41	18.43 ± .54
n-propyl ether		
carbon monoxide	6.81 ± .20	6.63 ± .32
methane	4.64 ± .13	4.83 ± .19
ethane	.70 ± .14	.54 ± .08
ethylene	5.36 ± .18	5.37 ± .19
acetylene	15.28 ± .30	14.36 ± .28
iso-propyl ether		
carbon monoxide	10.24 ± .17	10.24 ± .18
methane	4.64 ± .12	4.95 ± .17
ethane	1.99 ± .15	1.63 ± .25

1×10^{-3} I_2		5×10^{-3} I_2	
a	b	a	b
6.92 ± .26	6.95 ± .18	7.10 ± .09	6.88 ± .09
14.18 ± .17	15.70 ± .32	15.09 ± .12	14.29 ± .12
16.08 ± .43	15.89 ± .41	16.14 ± .52	16.72 ± .25
1.67 ± .07	1.80 ± .06	1.51 ± .11	1.46 ± .05
.95 ± .06	1.05 ± .08	.54 ± .03	.73 ± .02
12.43 ± .41	12.79 ± .33	10.92 ± .40	11.29 ± .40
21.03 ± .54	21.24 ± .43	20.63 ± .37	20.12 ± .77
6.50 ± .33	6.59 ± .33	6.98 ± .02	7.12 ± .02
2.54 ± .18	2.83 ± .18	2.53 ± .11	2.34 ± .10
.38 ± .04	.37 ± .07	.39 ± .03	.35 ± .01
4.34 ± .08	4.88 ± .08	4.54 ± .13	4.71 ± .13
15.13 ± .35	15.36 ± .14	14.68 ± .01	15.29 ± .04
9.90 ± .20	9.94 ± .14	10.22 ± .17	10.72 ± .21
2.20 ± .10	2.34 ± .12	1.95 ± .02	1.74 ± .02
.98 ± .17	1.01 ± .12	.68 ± .03	.66 ± .03

Table 9. (Continued)

System product	Unscavenged	
	[a]	[b]
iso-propyl ether cont.		
ethylene	10.74 ± .29	11.57 ± .16
acetylene	20.04 ± .31	19.97 ± .33
tetrahydrofuran		
carbon monoxide	10.71 ± .24	11.08 ± .09
methane	4.67 ± .11	4.93 ± .14
ethane	.41 ± .07	.33 ± .10
ethylene	2.64 ± .18	2.46 ± .17
acetylene	16.51 ± .31	14.76 ± .49
para-dioxane		
carbon monoxide	17.78 ± .19	19.38 ± .14
methane	3.76 ± .11	3.92 ± .19
ethane	.50 ± .15	.49 ± .09
ethylene	2.60 ± .16	2.64 ± .11
acetylene	14.67 ± .64	15.52 ± .41

1×10^{-3} I_2		5×10^{-3} I_2	
a	b	a	b
9.95 ± .17	10.17 ± .24	9.23 ± .03	9.51 ± .03
20.12 ± .49	20.20 ± .38	18.63 ± .53	19.39 ± .53
10.72 ± .16	11.23 ± .14	10.71 ± .08	11.13 ± .18
2.51 ± .14	2.71 ± .13	2.47 ± .10	2.31 ± .06
.39 ± .09	.34 ± .05	.33 ± .05	.32 ± .02
1.86 ± .15	2.28 ± .10	2.14 ± .07	2.19 ± .02
16.48 ± .14	17.32 ± .21	16.12 ± .34	16.57 ± .44
18.85 ± .21	19.35 ± .41	19.67 ± .42	20.50 ± .48
2.17 ± .08	2.20 ± .06	2.06 ± .03	2.08 ± .03
.43 ± .05	.38 ± .03	.54 ± .04	.39 ± .05
2.11 ± .12	2.17 ± .06	1.91 ± .05	2.04 ± .06
14.37 ± .30	15.41 ± .59	15.16 ± .41	15.99 ± .43

insertion reactions of ^{11}C, ^{11}CH, and $^{11}CH_2$ into C-H bonds. The yield values indicate that the reactions are generally complex with the initial insertion step affected by the relative insertion probabilities into primary, secondary, and tertiary C-H bonds and the energetics of the fragmentation processes required to free the labeled products from the various intermediates.

The carbon monoxide yields for the complete list of alcohols and ethers studied in this laboratory are listed in Table 10. The yield of this product varies systematically with the structure of the oxygen containing molecule (vide infra) suggesting a simpler, perhaps more direct reaction than those which produce hydrocarbon products. The energetics of deoxygenation of these compounds by atomic carbon are favorable in view of the large energy (257 kcal/mole) of the carbon-oxygen bond formed in the process. In all cases the formation of a molecule of carbon monoxide and the accompanying carbene or radical fragments, as illustrated in Equation 22, is exothermic by 50-100 kcal/mole. This accounts in part for the high yields of carbon monoxide by carbon atoms produced at near thermal energies as well as in the recoil system.

It has been found that the carbon monoxide yield for all the alcohols and ethers studied can be calculated on the basis of a simple site model. The various structural

Table 10. Carbon monoxide yield and site model results

Compound	Experimental CO yield %	Production sites	Total sites	Calculated CO yield %	Yields[a]
methanol	24.5 ± 0.3	1.00	4.00	25.0	16.8
ethanol	17.3 ± 0.6	1.00	6.00	16.7	14.3
propanol	12.7 ± 0.2	1.00	8.00	12.5	11.7
i-propanol	14.7 ± 0.2	1.20	7.98	15.0	12.8
n-butanol	9.9 ± 0.2	1.00	10.00	10.0	
i-butanol	10.4 ± 0.2	1.00	9.78	10.2	
s-butanol	12.4 ± 0.2	1.20	9.98	12.0	
t-butanol	16.0 ± 0.4	1.71	10.71	16.0	18.8
ethyl ether	9.4 ± 0.1	.97	10.97	8.8	
propyl ether	6.5 ± 0.3	.97	14.97	6.5	
i-propyl ether	9.9 ± 0.2	1.49	15.05	9.9	
tetrahydrofuran	10.9 ± 0.2	.97	8.97	10.8	
dioxane	19.1 ± 0.3	1.94	9.94	19.5	

[a] Skell and Harris (80).

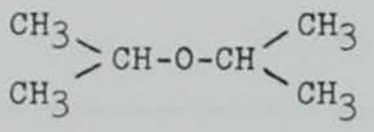
types of C-H bonds and O centers are listed in Table 11. Site values for these units were determined using the COFIT computer program discussed in the experimental section by allowing each of these seven variables to assume that value which minimizes the average deviation between the experimental results and those calculated from these site values in the manner illustrated below. The site values were normalized by assigning the value of 1.00 to a C-H bond of a - CH_3 or - CH_2-structural element.

$$\text{Yield}_{CO} = \frac{\text{production site value}}{\text{total sites in the molecule}} \times 100 \qquad (25)$$

for n-propanol $CH_3CH_2CH_2OH$

$$Y_{CO} = \frac{1.00}{7 \times 1.00 + 1 \times 1.00} \times 100 = 12.5\%$$

for iso-propyl ether



$$(CH_3)_2CH\text{-}O\text{-}CH(CH_3)_2$$

$$Y_{CO} = \frac{1.49}{12 \times 1.00 + 2 \times .78 + 1 \times 1.49} \times 100 = 9.9\%$$

The site model as presented to this point is admittedly quite abstract and somewhat undirected. However, a discussion of the results will hopefully clarify the approach and justify the mathematical treatment.

The final site values are listed in Table 11. The error limits show how precisely the values can be determined

Table 11. Molecular sites and site values

Molecular site	Site value
CO production sites	
O in $-CH_2OH$	1.00 ± .01
O in $>CHOH$	1.20 ± .06
O in $-\overset{\mid}{\underset{\mid}{C}}OH$	1.71 ± .05
O center of $-CH_2OCH_2-$	0.97 ± .02
O center of $>CHOCH<$	1.49 ± .09
Competing sites	
C-H bond of $-CH_3$ or $-CH_2-$	1.00 ± .02
C-H bond of $>CH-$	0.78 ± .33

by the data being considered. The values are the average values for a particular kind of site wherever it appears in this set of molecules as determined by the best overall agreement with the experimental results. The calculated ^{11}CO yields are listed in Table 10 along with the production sites and total sites used in the calculations illustrated above. The difference between calculated and experimental values is approximately the same as the uncertainty in the experimental values. The close agreement using seven parameters is perhaps not surprising but the fact that any such model is successful in calculating the yield of a product of recoil carbon reflects the unusual simplicity of the reaction leading to that product.

The relative site values of the oxygen groups are of particular importance. The primary -OH group has a value of 1.00 resulting in a regular decrease in carbon monoxide yield for the series of primary alcohols. The secondary -OH group of i-propanol and s-butanol has a higher site value (1.20) indicating that it is 20% more productive in the deoxygenation reaction. In t-butanol the -OH site value is even higher (1.71), or more than 70% greater than for primary -OH groups. The site value for the oxygen center of unbranched ethers (0.97) is very similar to the primary -OH value suggesting the independence of the deoxygenation process toward the bond energies by which the oxygen atom is bound. Iso-propyl ether presents another example of the effect of carbon chain branching resulting in increased reactivity toward deoxygenation.

As was pointed out this simple site model approach does not work even in modified forms for the yields of the other fragmentation products in these systems. In carbon recoil studies the mechanisms are generally so complex and so diverse with several reaction routes leading to most products that structural correlations are impossible with the expected structural dependence masked by additional and/or interfering reactions. There are several reasons for such complex mechanisms including the wide range of carbon atom energies, the interaction of radiation produced species with reaction intermediates, and the high reactivity of the bare carbon atom with or without excessive kinetic energy. The radiation effects have been removed from the CO yields discussed here by the presence of $\sim 1 \times 10^{-3}$ mole fraction iodine providing constant yields over a wide range of dose.

The correlation of carbon monoxide yield by a simple site model suggests some interesting conclusions about the formation reaction. The carbon atom is well known as a strong electrophile and seeks out areas of high electron density. Generally, from hydrocarbon studies, it attacks C=C and C-H bonds in order to achieve normal bonding. Apparently deoxygenation is a very efficient process in view of the high yields observed in spite of a large number of other reactions competing for the carbon atoms. Due to the success of the simple model one would conclude that there is only one reaction pathway contributing to CO production, a simple low energy collision reaction. There is definite evidence that the carbon atom is attacking the nonbonding pairs of electrons on oxygen. The oxygen of the ether molecule is very similar in reactivity toward ^{11}C atoms even though it is bonded to two carbon atoms. Increased branching of the carbon chain increases the oxygen site value apparently reflecting increased electron availability by the inductive effect of alkyl groups.

The energy released from the formation of the strong $C \equiv O$ bond becomes available to the deoxygenation process as the separation of the CO unit from the remainder of the molecule progresses. The breakage of the bonds necessary to free the CO molecule does not seem to be an important factor in determining the reactivity of a given oxygen group suggesting that deoxygenation occurs with carbon atoms without excessive kinetic energy. Skell's experiments with thermal and sub-thermal carbon species support this hypothesis and provide the capability for observing the behavior of the molecular fragments resulting from deoxygenation of a wide variety of oxygen containing molecules. In studies with aldehydes and ketones (128) Skell and Plonka have shown that the resulting ketenes lead to reaction products quantitatively similar to the products of these ketenes generated by thermal decomposition of diazirines and diazo compounds. There is a close similarity in products despite great differences in temperature ~ 350°, medium, and precusors. Since deoxygenation apparently generates free carbenes Skell concludes that it must be catalogued as a low-energy, thermal process. The predominant products from the carbenes are olefins and cyclopropanes presumably formed by intramolecular reactions through a singlet structure. Moritani _et al._ (129) have recently reported direct evidence that singlet states are required for these reactions.

Comparison of results of carbon vaporizations from resistively heated carbon and arc vaporizations is interesting. The thermal method is known to produce predominately ground-state carbon species (^3P for C_1). The carbon monoxide yield is dramatically lower with these carbon species than it is from arc vaporization where electron bombardment in the arc plasma produces a greater abundance of excited carbon species (^1D and ^1S for C_1). Deoxygenation by singlet carbon is consistent with spin conservation since a singlet carbene is generated with the production of each molecule of carbon monoxide. The carbenes generated by deoxygenation exhibit a totally different chemistry from the carbenes generated by carbon atom insertion into alkane C-H bonds in the condensed phase (59, 130) further supporting the hypothesis of unusual carbene behavior due to excessive excitation energies discussed in the Introduction.

If these conclusions of Skell are to be applicable in the ^{11}C recoil studies presented here, the carbon monoxide yields from alcohols with vaporized carbon must be compared. The CO yields reported by Skell and Harris (80) are listed in the last column of Table 10 and represent the weight percentage of the total carbon vaporized, of which a minimum of 40% is atomic carbon. Although the absolute agreement is not good the same trends are evident, namely the decrease in yield for the primary alcohols and the higher than expected yields for the branched alcohols. Since the distribution of recoil carbon atoms among the several low-lying electronic states is presently not known, no direct comparison of the reactivity of the singlet states in these two experimental systems is possible. The trends suggest a strong similarity between the reactions producing carbon monoxide in the two systems.

In order to see if something other than a simple site model might apply an attempt has been made to relate the oxygen group reactivities to physically measurable properties of the molecules in question. Using the molecular refractivities and the best atomic refractivities of carbon and hydrogen averaged from many compounds, the atomic refractivity of the oxygen atom in each of the molecules studied was calculated. Although these results might be expected to reflect the polarizability and hence the electron availability of the oxygen atom none of the trends noted in the experimental data were apparent. Collision cross sections might also provide a logical explanation for the success of the site model since the fraction of total collisions occurring with the oxygen group might determine the CO yield. Accurate values of partial and total cross sections are not available and qualitative considerations suggest that cross sections would not be consistent with the larger yield of ^{11}CO from i-propyl ether than from ethyl ether in which the oxygen center certainly represents a larger fraction of the molecular cross section.

One concludes that the deoxygenation reaction is efficient and predictable. It is strongly dependent on electronic factors. An attractive possibility is a one step process by direct collision with a site sufficiently reactive to be probable even without excessive collision energy. This would account for the high yields, and the one path simplicity of the mechanism would account for the effective calculation method involving simple site and bond counting. Additional information about the mechanism will be difficult to obtain in the liquid state where variable parameters are very limited.

C. Product Identification and Mechanisms in Methanol

Palino and Voigt (28) have presented a rather complete study of the methanol system. Using reactions of ^{11}C, ^{11}CH, $^{11}CH_2$, and $^{11}CH_3$ they attempted to account for the production of the wide variety of labeled products in this system using detailed reaction schemes. The primary reactions are deoxygenation, insertion into C-H bonds, and insertion into the O-H bond producing excited intermediates which react to stable products by rearrangement, hydrogen loss or pickup, collisional deactivation, or bimolecular reaction with the solvent or radiation produced species. Additional studies of the methanol system are reported in this thesis in an attempt to clarify and evaluate some of the proposed reaction schemes. The strong dose dependence of the yields of carbon monoxide and glycolaldehyde is discussed in a separate section.

It is intended that the discussion of mechanisms here will be complete enough to convey the significance of the new results but reference is recommended to the Palino and Voigt paper for a presentation of the complete reaction scheme and product yields. The results to be discussed are presented in Table 12. For those products studied in both this work and in the Palino study the results agree well within experimental error eliminating the need to routinely redetermine yield values. Selected results from Palino's work are included in Table 12 and are so designated.

The primary concern is the behavior of the C-H insertion intermediate which is the precursor of several products. Since a wide variety of reaction paths were already ascribed

Table 12. Yields of selected products from methanol systems

Product	-[a]	-[b]	1×10^{-3} I_2
methyliodoacetate	-	-	2.05
methylacetate	3.57[d]	3.05[d]	trace
acetaldehyde	~ 3.9[d]	0.85[d]	-
1,2-propanediol	5.73[d]	8.50[d]	-
dimethoxyethane	-	-	3.03
2,2-dimethoxyiodoethane	-	-	7.9
2-iodoethanol	-	-	0.86

[a] Dose (eV/molecule) = 0.009.

[b] Dose (eV/molecule) = 0.036.

[c] Yield of corresponding bromo- products.

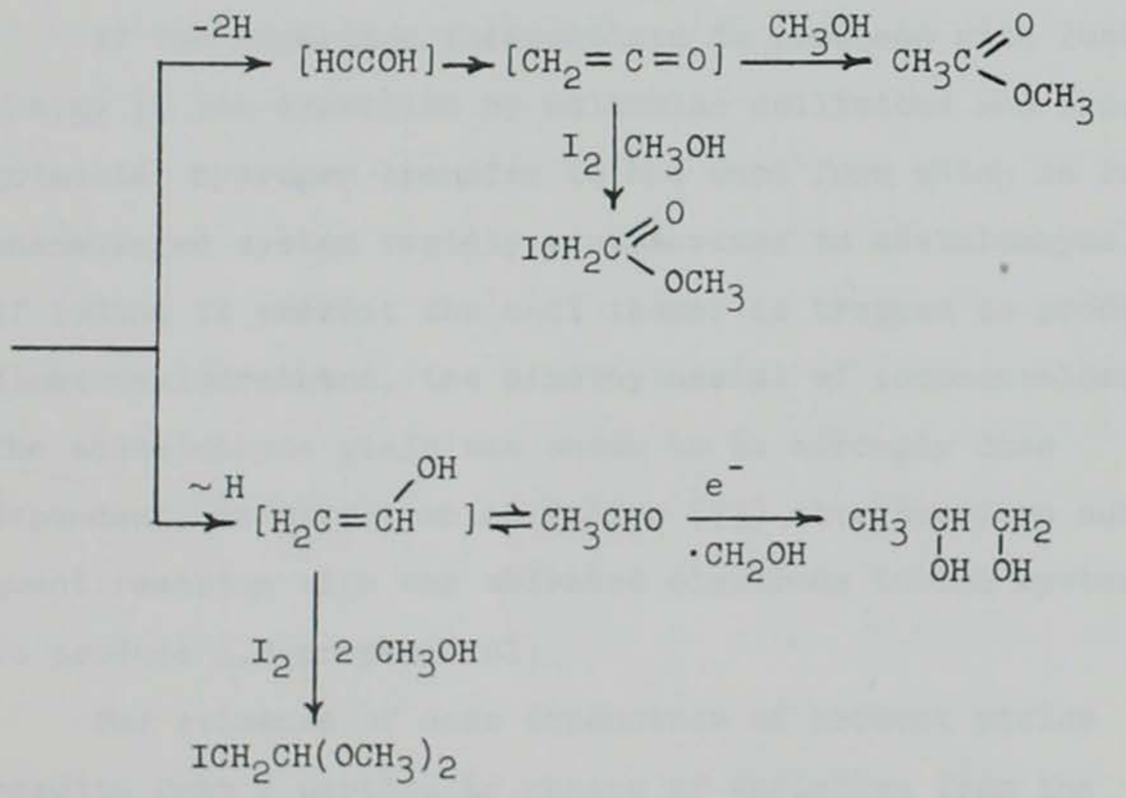
[d] Results from Palino and Voigt (28).

[e] Yield with acetaldehyde present during irradiation.

2×10^{-3} I_2	5×10^{-3} I_2	1×10^{-3} Br_2 [c]	Other
2.47	3.45	2.7	
trace	-		
			7.3 [e]
			1.2 [e]
8.3	9.4	9.4	
0.90	1.3	1.3	

to the C-H intermediate Palino and Voigt designated an additional primary interaction species $[C_2H_4O]^*$ as the precursor of methylacetate and acetaldehyde. The results presented here suggest that an indefinite intermediate is not required and the resultant products follow logically from the C-H insertion intermediate. The proposed scheme is shown in Equation 26.

$$CH_3OH + {}^{11}C \rightarrow [H-{}^{11}C-CH_2OH]^* \longrightarrow$$



(26)

The insertion intermediate $[H-{}^{11}C-CH_2OH]^*$ can result from the interaction of methanol with carbon atoms over a wide range of energy. It is suggested that enough energy is deposited locally in some of the insertions to result in the loss of both hydrogen atoms from the methanol carbon atom producing an alkynol intermediate which rapidly collapses to ketene. In the unscavenged system the ketene is efficiently trapped by methanol to form the ester, methylacetate. In the scavenged system iodine removes the ketene, producing methyliodoacetate. The quantitative replacement of the ester by the iodo product is shown in Table 12. The minor dependence of yield on iodine concentration is indicative of a competitive reaction.

If the insertion intermediate is produced with less energy it can stabilize by molecular collisions and intramolecular hydrogen transfer to the enol form which in the unscavenged system rapidly tautomerizes to acetaldehyde. If iodine is present the enol isomer is trapped to produce dimethoxyiodoethane, the dimethylacetal of iodoacetaldehyde. The acetaldehyde yield was shown to be strongly dose dependent, an effect which Palino (73) attributed to subsequent reaction with the solvated electrons in the system to produce 1,2-propanediol.

The evidence of dose dependence of product yields results from a particular choice of variables from the interrelated variables, dose, dose rate, and irradiation time discussed in the experimental section of this thesis. The experimental variables are in practice the irradiation time and the dose rate, which depends on the operational characteristics of the synchrotron for a particular irradiation. However, the total dose received by the sample can be accurately determined by the quantity of ^{11}C produced during the irradiation period. Dose dependence would apparently account for systematic yield changes due to reactions of radiation produced species with labeled products, the interference by radical reactions becoming more significant with increasing dose. Closer examination of the mathematics involved indicates that this explanation is not the most direct approach. The yield of any product (see Experimental section) is the fraction of the total carbon activity of the sample measured after the irradiation. Carbon-11 is produced at a constant production rate dependent on the synchrotron beam intensity (dose rate), but decays by positron emission with its radio-decay constant λ. Thus the carbon activity does not increase linearly with irradiation time but instead follows the usual isotope production curve, $A = P (1 - e^{-\lambda t})$, where A is the activity, P the production rate, and t the irradiation time. Since the same decay constant obtains for the carbon labeled products the yield of most products is not time dependent. However if radical reactions remove some of the product molecules the yield must decrease, but the nature of the change is not obvious. The radicals are present at a steady state concentration dependent on the reaction medium and the intensity of the radiation beam. They are present at a concentration much higher than the concentration of ^{11}C labeled products. Radical reactions would then be expected to remove a constant fraction, α, of the ^{11}C labeled product present at any time. Therefore the activity attributed to the product would increase during the irradiation by the modified production formula, $A = P\,(1 - e^{-(\lambda+\alpha)t})$ and hence the yield would show a nonlinear decrease with increasing irradiation time. Since at relatively constant dose rate ("average beam intensities") the irradiation time and the total dose are proportional, the Palino dose interpretation is qualitatively valid but does not reveal the more fundamental aspects of the reaction system.

The yield of acetaldehyde is an example of this time dependence. Figure 1 shows the yield values of acetaldehyde in the methanol system as a function of time. The dose rate was relatively constant for these samples varying less than 50% for the set and less than 10% during any irradiation. The curves are calculated from the following equation,

$$\text{Yield} = \frac{\frac{P_1}{\lambda+\alpha}\,(1 - e^{-(\lambda+\alpha)t})}{P_2\,(1 - e^{-\lambda t})} \qquad (27)$$

where α represents the fraction of acetaldehyde removed per minute of irradiation time by radiation species. The ratio

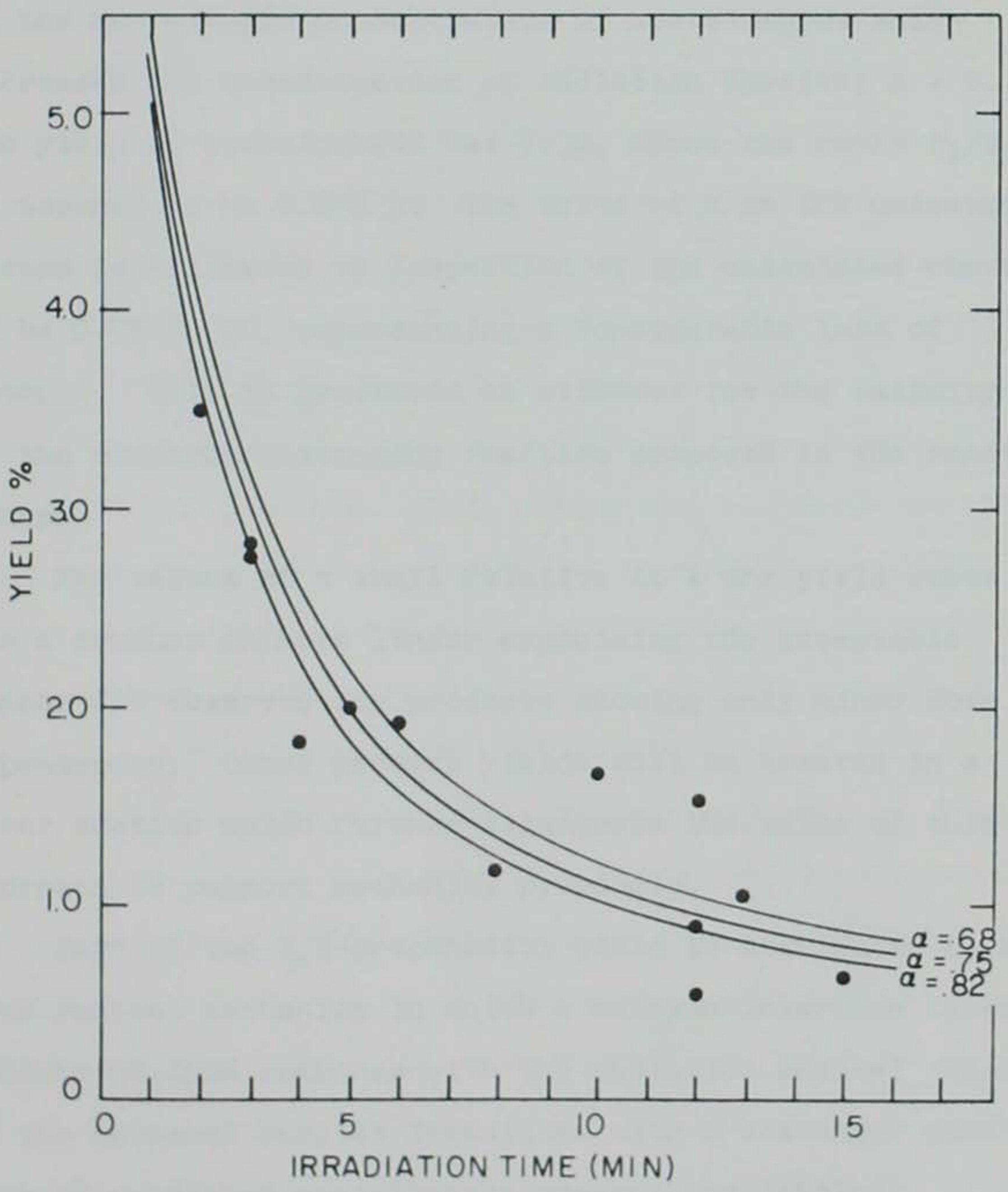


Figure 1. Acetaldehyde yield and calculated curves

of production rates, P_1/P_2, was determined from the yield of acetaldehyde from methanol samples to which nonlabeled acetaldehyde had been added before the irradiation. In this system the labeled product was statistically protected by the macroscopic concentration of acetaldehyde which decreased the concentration of radiation species; $\alpha = 0$. The yield of acetaldehyde was 7.3%, hence the ratio P_1/P_2 is assumed to be 0.073 λ. The value of α in the unscavenged system is estimated by inspection of the calculated curves to be 0.75 ± .10, representing a considerable loss of product. This is presented as evidence for the validity of the electron scavenging reaction proposed in the reaction scheme.

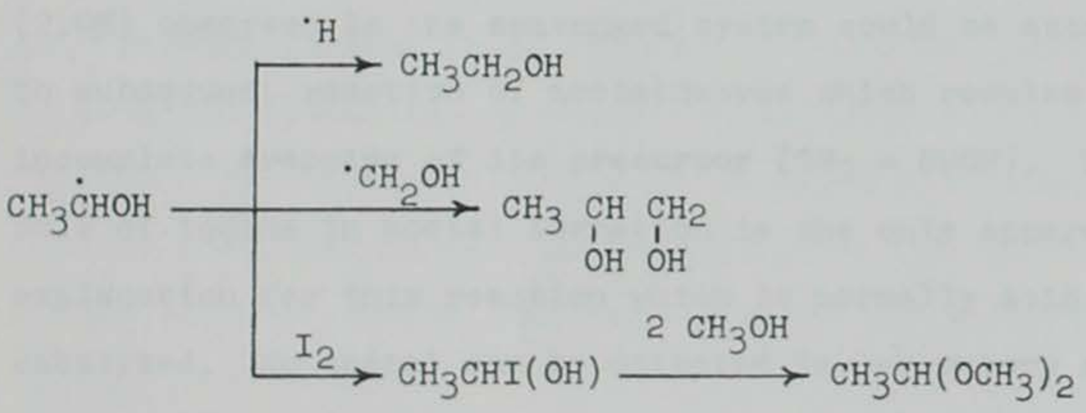
For values of α small relative to λ the yield curve for a product is more linear explaining the acceptable linear fit observed for products showing only minor dose dependences. Other product yields will be treated in a later section which further illustrate the value of this approach to support mechanism proposals.

Part of the 1,2-propanediol yield is attributed to a free radical mechanism in which a methyne insertion intermediate $CH_3\dot{C}HOH$ combines with the radiation radical $\cdot CH_2OH$. In the methanol samples irradiated with a scavenger quantity of unlabeled acetaldehyde present the labeled acetaldehyde is protected from conversion to 1,2-propanediol and the free radical mechanism contribution is then the 1.2% yield of labeled 1,2-propenediol. At the same time the acetaldehyde yield is increased to its production value of 7.3%. If this free radical contribution is subtracted from the 1,2-propanediol yield observed in unscavenged methanol, 7.1 - 1.2 = 5.9, conservation of products between the unscavenged and iodine scavenged systems supports the proposed reaction scheme. The yields of acetaldehyde (1.8%) and 1,2-propanediol (5.9%) are replaced by dimethoxyiodoethane which shows a dependence on iodine concentration, 7.9% at 1 x 10^{-3}, 8.3% at 2 x 10^{-3}, and 9.4% at 5 x 10^{-3}, reflecting the competitive character of the trapping reaction. This comparison of yields was made at a dose of 0.020 eV/molecule but is equally valid at other doses since acetaldehyde is smoothly converted to 1,2-propanediol with increasing dose while the scavenger product yield is independent of dose.

Support for the reactions proposed for another labeled free radical was obtained in this work. It was proposed by Palino and Voigt (28) that $\cdot CH_2CH_2OH$ combined with the radiation radical $\cdot CH_2OH$ to produce 1,3-propanediol in a reaction analogous to the radical formation of 1,2-propanediol discussed previously. If this were the case one would expect the replacement of this product by 2-iodoethanol in the scavenged system. To aid in the verification of this proposal methanol samples scavenged with bromine were examined. The corresponding 2-bromoethanol is considerably more stable with respect to thermal decomposition and has a considerably lower boiling point facilitating its elution from the chromatograph column and its detection in the counting cell. The 2-iodoethanol was later identified directly using a shorter column to lower the retention time. The yields of several bromo compounds are reported in Table 12 for the bromine scavenged system. They illustrate that the trapping reactions discussed here are not unique to iodine but are more general reactions of free radical scavengers. The agreement between the yields of these halogen compounds is further evidence for the quantitative removal of certain reaction intermediates. The yield of 2-iodoethanol (1.3%) apparently accounts for the loss of 1,3-propanediol (1.2%).

Bromine scavenger studies proved valuable in the identification of dimethoxyiodoethane which is not commercially available. Identification of dimethoxybromoethane in the bromine scavenged system led to laboratory preparations of the iodo compound. Two independent preparation techniques were used. Direct exchange of iodide for bromide was accomplished by equilibration of a solution of NaI and dimethoxybromoethane in acetone. A more fundamental synthesis was suggested by the formation mechanism proposed for the recoil system and its success lends considerable support to that proposal. Methylvinylether, the methoxy analog of the enol intermediate proposed, $[H_2C{=}CHOH]$, was shown to produce dimethoxyiodoethane in an iodine solution of methanol at 0° C. From both preparations aliquots of the reaction mixture were injected onto the chromatograph column with an irradiated sample and the unknown activity peak was identified by retention time without purification of the preparation product.

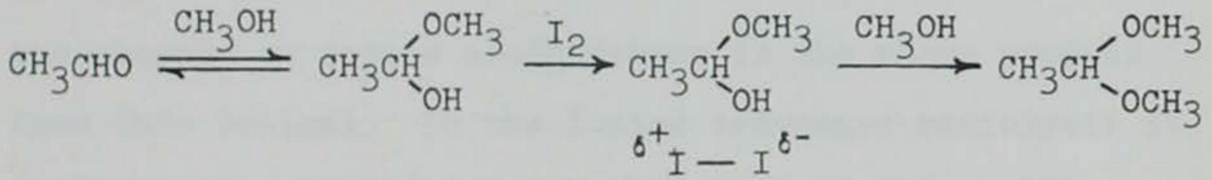
Another of the Palino mechanisms was examined. Since there is no 1,2-propanediol formed in the iodine scavenged system the fate of the precursor radical, $CH_3\dot{C}HOH$, is of interest. The following reaction was proposed.



$$\begin{aligned} CH_3\dot{C}HOH &\xrightarrow{\cdot H} CH_3CH_2OH \\ CH_3\dot{C}HOH &\xrightarrow{\cdot CH_2OH} CH_3\,\underset{OH}{CH}\,\underset{OH}{CH_2} \\ CH_3\dot{C}HOH &\xrightarrow{I_2} CH_3CHI(OH) \xrightarrow{2\ CH_3OH} CH_3CH(OCH_3)_2 \end{aligned} \qquad (28)$$

Formation of the acetal from the gem-iodohydrin is similar to the acetal formation steps in the preparation of dimethoxyiodoethanol except that nucleophilic attack by methanol must displace the OH group with the aid of iodine in the solution. Evidence will be presented that this reaction may be occurring to produce part of the observed dimethoxyethane yield.

The yield of dimethoxyethane (3.0%) is considerably greater than can be attributed to the replacement product of 1,2-propanediol (1.2%) resulting from the radical reaction. It has been shown that acetaldehyde reacts with methanol in the presence of iodine to produce the dimethyl acetal. A suggested mechanism is shown below.



$$CH_3CHO \overset{CH_3OH}{\rightleftharpoons} CH_3CH\begin{matrix}OCH_3\\OH\end{matrix} \xrightarrow{I_2} \underset{^{\delta+}I-I^{\delta-}}{CH_3CH\begin{matrix}OCH_3\\OH\end{matrix}} \xrightarrow{CH_3OH} CH_3CH\begin{matrix}OCH_3\\OCH_3\end{matrix}$$

(29)

If this reaction is occurring most of the dimethoxyethane (2.0%) observed in the scavenged system could be attributed to subsequent reaction of acetaldehyde which results from incomplete trapping of its precursor [$CH_2 = CHOH$]. The role of iodine in acetal formation is the only apparent explanation for this reaction which is normally acid catalyzed. No acetal can be detected in laboratory experiments in the absence of iodine and the yield of dimethoxyethane is below the detection limits in the unscavenged recoil system. In the presence of iodine dimethoxyethane is produced in good yield in the recoil system and no acetaldehyde is observed. Acetal formation in the corresponding ethanol solution has been verified, suggesting that the Lewis acid strength of iodine is perhaps enhanced by the solvent molecules.

The behavior of the $CH_3\dot{C}HOH$ radical in alcohol-iodine solutions would be useful in testing this hypothesis as pertains to Equation 28 in which displacement of the iodine would produce the same hemiacetal as in Equation 29 and would result in acetal formation. Radiolysis studies of ethanol, in which $CH_3\dot{C}HOH$ is reported to be the predominant primary intermediate (131), have been inconclusive since in the absence of iodine acetaldehyde is the major product from this radical. In the iodine scavenged radiolysis it is impossible to distinguish that part of the acetal resulting from acetaldehyde from that having the $CH_3\dot{C}HOH$ radical as its direct precursor.

The identification of several products and investigation of selected mechanisms in the methanol systems was a time consuming part of this study. It is hoped that the results further the understanding of recoil carbon reactions in methanol and encourage additional study in this interesting system.

D. Kinetic Analysis in the Methanol System

1. Reactions of the solvated electron

The yields of carbon monoxide, glycolaldehyde, and acetaldehyde in the unscavenged methanol system show unusual dependence on the length of the irradiation period. It was shown in a previous section that for acetaldehyde a simple scavenging reaction by a radiation produced species would account for the decreasing yield by removal of a constant fraction of the labeled acetaldehyde present at any time during the irradiation. Other products in the methanol system show less pronounced time dependence suggesting the removal of a much smaller fraction of the products resulting in nearly linear decreases with increasing irradiation time. Such decreases for unsaturated hydrocarbon products have been attributed (73) to reactions of hydrogen atoms resulting in increased yields of more-saturated products with increased time. The yields of some products, such as ethanediol, 1,3-propanediol, and ethanol, are attributed at least in part to combination of labeled radicals with the predominant radiation species in methanol, $\cdot CH_2OH$ and $\cdot H$, and show increases in yield with irradiation time. These minor dependences can be considered normal behavior for labeled products in methanol, and similar effects are shown in the results reported for other systems in Table 9.

The carbon monoxide production site model is based on results of samples scavenged with iodine in which the carbon monoxide yield is independent of irradiation time for all the compounds studied. In all cases the carbon monoxide yield is somewhat higher if iodine is present during the irradiation, but for unscavenged methanol the carbon monoxide yield falls from values near the scavenged yield for short irradiation times to values only one-third as large for irradiation times of 20-30 minutes. The yields of acetaldehyde and glycolaldehyde show similar time dependences in the same unscavenged system. It will be shown that all three of these products are removed by reaction with a radiation species, the solvated electron, which is important in the radiation chemistry of water and alcohols but which affects only selected recoil products in methanol for reasons to be presented.

The discovery of and development of ideas concerning the solvated electron is an interesting part of modern radiation chemistry. In 1947 Lea (132) proposed that electrons in irradiated water escaped the parent ion. Beginning with the work of Baxendale and Hughes (133) in 1958 evidence rapidly accumulated supporting the existence of e_{aq}^-. It was demonstrated that the major reducing species in irradiated water has unit charge (134, 135) and the absorption spectrum of the transient hydrated electron was observed in pulse radiolyzed aqueous solutions (136). The rate constants of reactions of e_{aq}^- and other solvated electrons with a large number of compounds have been measured using the technique of pulse radiolysis and have been conveniently tabulated (137). An intensive review of the current understanding of the solvated electron and its reactions has recently been prepared (138) and is recommended as an indepth summary of the subject.

The results of reactions of e^-_{aq} with more than 300 compounds suggest that the reactivity of different chemical species toward e^-_{aq} is a function of the availability of a vacant orbital on the substrate as well as of the change in free energy on incorporation of an additional electron. The compounds carbon monoxide and acetaldehyde are among the more reactive toward e^-_{aq} with bimolecular rate constants 1×10^9 and 3.5×10^9 $M^{-1}sec^{-1}$. The rate constant for glycolaldehyde has apparently not been determined although all the simple aldehydes and ketones show similar reactivities, with the exception that formaldehyde is about two orders of magnitude less reactive. The low reactivity of formaldehyde, and its precursor radical $\cdot CH_2OH$ in the radiolysis of methanol, coupled with the low reactivity of methanol itself toward e^-_{solv} ($k < 10^4$ $M^{-1}sec^{-1}$) makes methanol an ideal solvent for the study of the solvated electron. The anomalous behavior of formaldehyde provides the reason why reactions of the solvated electron have been observed with recoil products in methanol but not in other systems. In the radiation chemistry of ethanol, for example, large quantities of acetaldehyde are produced, $G = 3.14$ (131). Acetaldehyde effectively removes the solvated electron, G = 1.0 (138, p. 39), eliminating its effects on yields in recoil studies. In methanol radiolysis the only product which can significantly reduce the concentration of solvated electrons is carbon monoxide, G = 0.26, which due to its low concentration would only be important in extended irradiations.

The rates of e^-_{aq} reactions have been used in the preceding discussion since these values have been determined for a wide variety of compounds. Very similar rate constants for the solvated electron in methanol and ethanol have been reported for some of the same compounds. For example, the rate constants for O_2 with the various solvated electrons are 2.0×10^{10} for water and 1.9×10^{10} for both methanol and ethanol (138, p. 41). Although such close agreement cannot be assumed for all compounds no significant differences have been reported.

The subsequent reactions of the molecular ions formed in the e^-_{solv} reaction have not been as thoroughly studied. The work of Weiss (139) is of particular interest and is the basis for the reaction proposals to be made here. He reported the formation of glycolic acid by the combination of the $\cdot CO_2^-$ radical ion with the methanol radical $\cdot CH_2OH$ in the radiolysis of aqueous methanol solutions with a G value of 2.7. Similarly $\cdot COH$ combines with $\cdot CH_2OH$ to produce glycolaldehyde. The radical $\cdot COH$ could be formed by the reaction of CO with e^-_{solv} followed by neutralization or by the combination of CO with ·H. The hydrogen atom reaction is apparently unimportant in methanol since similar concentrations of ·H are present during the irradiation of the other alcohols in which the carbon monoxide yields show little time dependence. The reactions of the solvated electron and the molecular ions resulting from its reactions with carbon monoxide and glycolaldehyde will be used to explain the time dependent yields of these products in the recoil studies of methanol.

The following reactions form the basis of a treatment used to calculate the time dependence of the yields of carbon monoxide and glycolaldehyde in the unscavenged methanol system.

$$CH_3OH + \gamma \xrightarrow{k_4} {}^{11}C\text{-products} \qquad (30)$$

$$CH_3OH + {}^{11}C \xrightarrow{k_1} {}^{11}CO \qquad (31)$$

$$CH_3OH + {}^{11}C \xrightarrow{k_5} CH_2(OH){}^{11}CHO \qquad (32)$$

$$^{11}CO + e^-_{solv} \xrightarrow{k_2} CH_2(OH)CHO \qquad (33)$$

$$CH_2(OH){}^{11}CHO + e^-_{solv} \xrightarrow{k_3} \text{unidentified product} \qquad (34)$$

Equation 30 represents the total production of ^{11}C-products by the synchrotron irradiation. The rate of production, denoted R_4, is independent of time and depends only on the beam intensity, dose rate. The rate of production of carbon monoxide, $R_1 = k_1\ [^{11}C]\ [CH_3OH]$, will be the same function of dose rate as R_4, since the rate constant k_1 and the methanol concentration are constant for all the irradiations while $[^{11}C]$ and the total production of ^{11}C-products depend on the beam intensity in the same way. Equation 32 represents the direct production of glycolaldehyde which was necessitated by the residual yield of this product in methanol samples to which scavenger quantities of glycolaldehyde were added before the irradiation. Under these conditions Reaction 33 would be eliminated by removal of e^-_{solv}. The observed glycolaldehyde yield might be attributed to the combination of $\cdot{}^{11}CHO$, produced by deoxygenation of methanol by methyne ^{11}CH, with $\cdot CH_2OH$ radicals which would not be removed by the glycolaldehyde scavenger. No additional evidence for or against deoxygenation by methyne has been reported. The rate of glycolaldehyde production by this direct reaction sequence, $R_5 = k_5\ [^{11}C]\ [CH_3OH]$, is similar to R_1 and R_4 in that it is independent of irradiation time but dependent on the rate of ^{11}C production.

The e^-_{solv} reactions, Equations 33 and 34, may be treated as pseudo-first order reactions since $K_2 = k_2\ [e^-_{solv}]$ and $K_3 = k_3\ [e^-_{solv}]$ are time independent. These constants may show different dose rate dependences from R_1, R_4, and R_5 since $[e^-_{solv}]$ and $[^{11}C]$ are not necessarily affected identically by changes in dose rate. A brief evaluation of this effect will also be presented.

With the use of Reactions 30 through 34 and the production rates previously discussed the expected time dependence of the ^{11}CO yield at a fixed dose rate can be determined by solving the prescribed rate equation.

$$\frac{d\,[^{11}CO]}{dt} = R_1 - \lambda\,[^{11}CO] - K_2\,[^{11}CO] \qquad (35)$$

$$[^{11}CO] = \frac{R_1}{\lambda + K_2}\,[1 - e^{-(\lambda + K_2)\,t}] \qquad (36)$$

Since the concentration of any ^{11}C labeled product relative to the concentration of the total ^{11}C product concentration is the yield of that product, the yield of ^{11}CO can be written as

$$Y_{^{11}CO} = \frac{\frac{R_1}{\lambda + K_2}\,[1 - e^{-(\lambda + K_2)\,t}]}{R_4\,(1 - e^{-\lambda t})} \qquad (37)$$

Equation 37 is of exactly the same form as Equation 27 for acetaldehyde, for which the development was intentionally brief in the methanol mechanism section.

In the iodine scavenged system $[e^-_{solv}]$ may be taken as zero, hence $K_2 = 0$ and the ratio R_1/R_4 can be evaluated under these conditions from the ^{11}CO yield, 25%.

$$Y^{scav}_{^{11}CO} = \frac{\frac{R_1}{\lambda}\left(1 - e^{-\lambda t}\right)}{R_4\left(1 - e^{-\lambda t}\right)} = \frac{R_1}{\lambda R_4} \tag{38}$$

Substituting this ratio, $R_1/R_4 = 0.25\ \lambda$, into Equation 37 results in an equation for the yield of ^{11}CO as a function of time and the rate of ^{11}CO loss by the e^-_{solv} reaction.

$$Y_{^{11}CO} = \frac{\frac{0.25\ \lambda}{\lambda + K_2}\left(1 - e^{-(\lambda + K_2)\ t}\right)}{\left(1 - e^{-\lambda t}\right)} \tag{39}$$

Figure 2 shows the carbon monoxide yield points as a function of time at a dose rate of 1.9×10^{-3} eV/molecule·min. The curves are determined by substituting selected values of K_2 into Equation 39. Although the experimental results show considerable scatter a relatively unique value of K_2 can be chosen by visual inspection. It is suggested that K_2 decreases as the irradiation time exceeds about 10 minutes which could result from a build up of CO and other e^-_{solv} scavengers by radiation mechanisms previously noted. A decrease in $[e^-_{solv}]$ would be reflected directly in K_2. The best initial value K_2 is seen to be ~ .20 with a decrease of K_2 to ~ .10 after 10 minutes.

A similar but somewhat more complicated treatment for glycolaldehyde can be based on Reactions 30 through 34 with the following results.

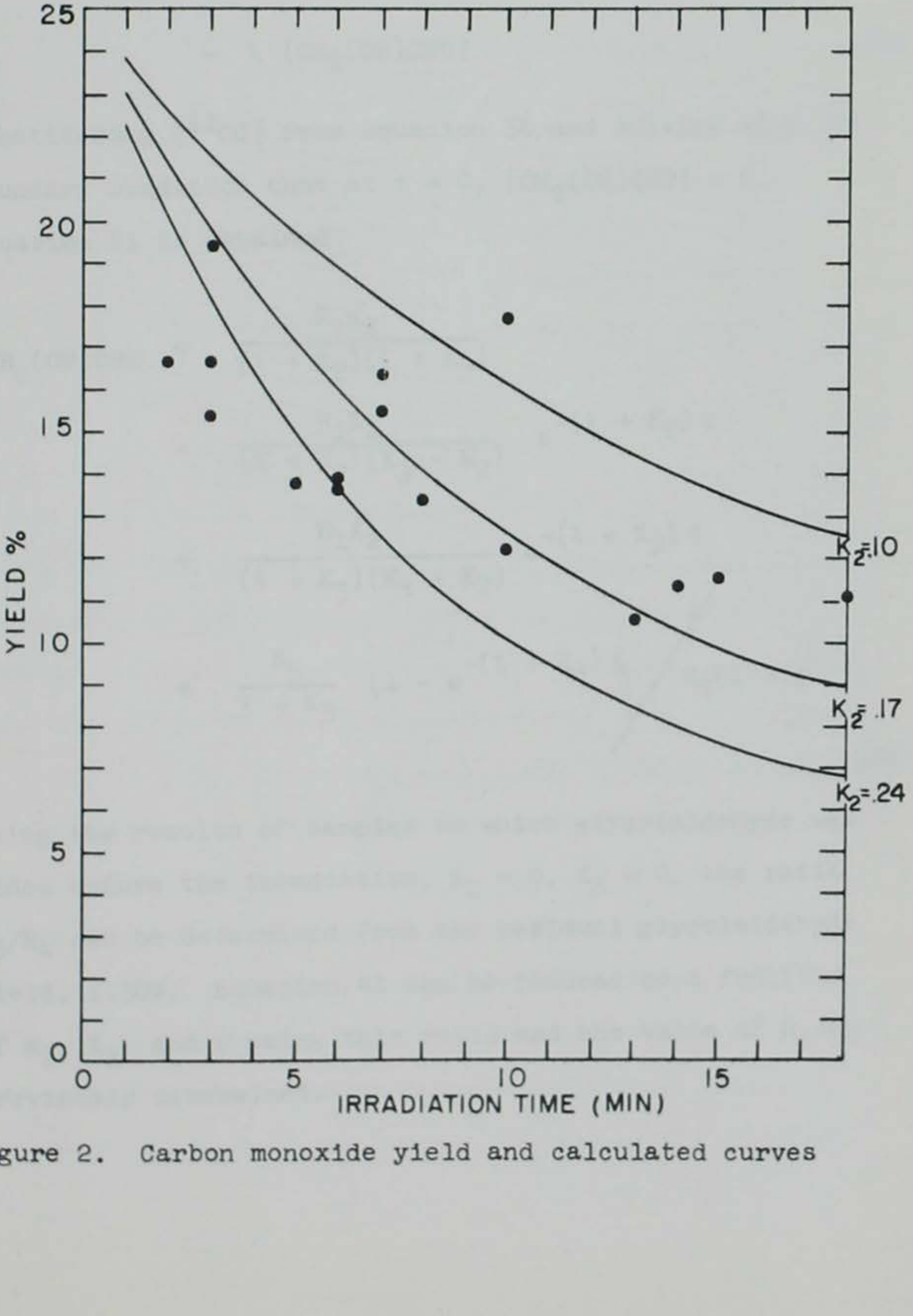


Figure 2. Carbon monoxide yield and calculated curves

$$\frac{d[CH_2(OH)CHO]}{dt} = R_5 + K_2\,[{}^{11}CO] - K_3\,[CH_2(OH)CHO] - \lambda\,[CH_2(OH)CHO] \qquad (40)$$

Substituting $[{}^{11}CO]$ from Equation 36 and solving with the boundary condition that at $t = 0$, $[CH_2(OH)CHO] = 0$, Equation 41 is obtained.

$$Y_{CH_2(OH)CHO} = \left[\frac{R_1K_2}{(\lambda + K_2)(\lambda + K_3)} - \frac{R_1K_2}{(\lambda + K_2)(K_3 - K_2)}\, e^{-(\lambda + K_2)\,t} + \frac{R_1K_2}{(\lambda + K_3)(K_3 - K_2)}\, e^{-(\lambda + K_3)\,t} + \frac{R_5}{\lambda + K_3}\,\left(1 - e^{-(\lambda + K_3)\,t}\right) \right] \Bigg/ R_4\left(1 - e^{-\lambda t}\right) \qquad (41)$$

Using the results of samples to which glycolaldehyde was added before the irradiation, $K_2 = 0$, $K_3 = 0$, the ratio R_5/R_4 can be determined from the residual glycolaldehyde yield, 1.38%. Equation 41 can be reduced to a function of K_2, K_3, and t using this ratio and the value of R_1/R_4 previously determined.

$$
\begin{aligned}
Y_{CH_2(OH)CHO} = \; & \frac{0.25\ K_2\ \lambda}{(\lambda + K_2)(\lambda + K_3)} \\
& - \frac{0.25\ K_2\ \lambda}{(\lambda + K_2)(K_3 - K_2)}\ e^{-(\lambda + K_2)\,t} \\
& + \frac{0.25\ K_2\ \lambda}{(\lambda + K_3)(K_3 - K_2)}\ e^{-(\lambda + K_3)\,t} \\
& + \frac{0.0138\ \lambda}{\lambda + K_3}\ (1 - e^{-(\lambda + K_3)\,t} \Bigg/ (1 - e^{-\lambda t}) \qquad (42)
\end{aligned}
$$

Figure 3 shows the glycolaldehyde yield points and curves calculated for selected values of K_2 and K_3. Due to the complexity of the reaction system and the experimental scatter the results are difficult to interpret. Best apparent values of the constants are $K_2 = .34$ to $.17$ and $K_3 = 1.5$ to 1.7. Since the calculated ^{11}CO yields used in this analysis are lower than experimental, K_3 is by necessity large. If a reduced $[e^-_{solv}]$ is reflected in the K_2 values from the CO treatment one would expect similar effects on the e^-_{solv} + glycolaldehyde reaction. The initial value of K_2 determined by glycolaldehyde formation is somewhat higher than the value from CO reduction. Since the two values of K_2 both represent the rate of Reaction 33

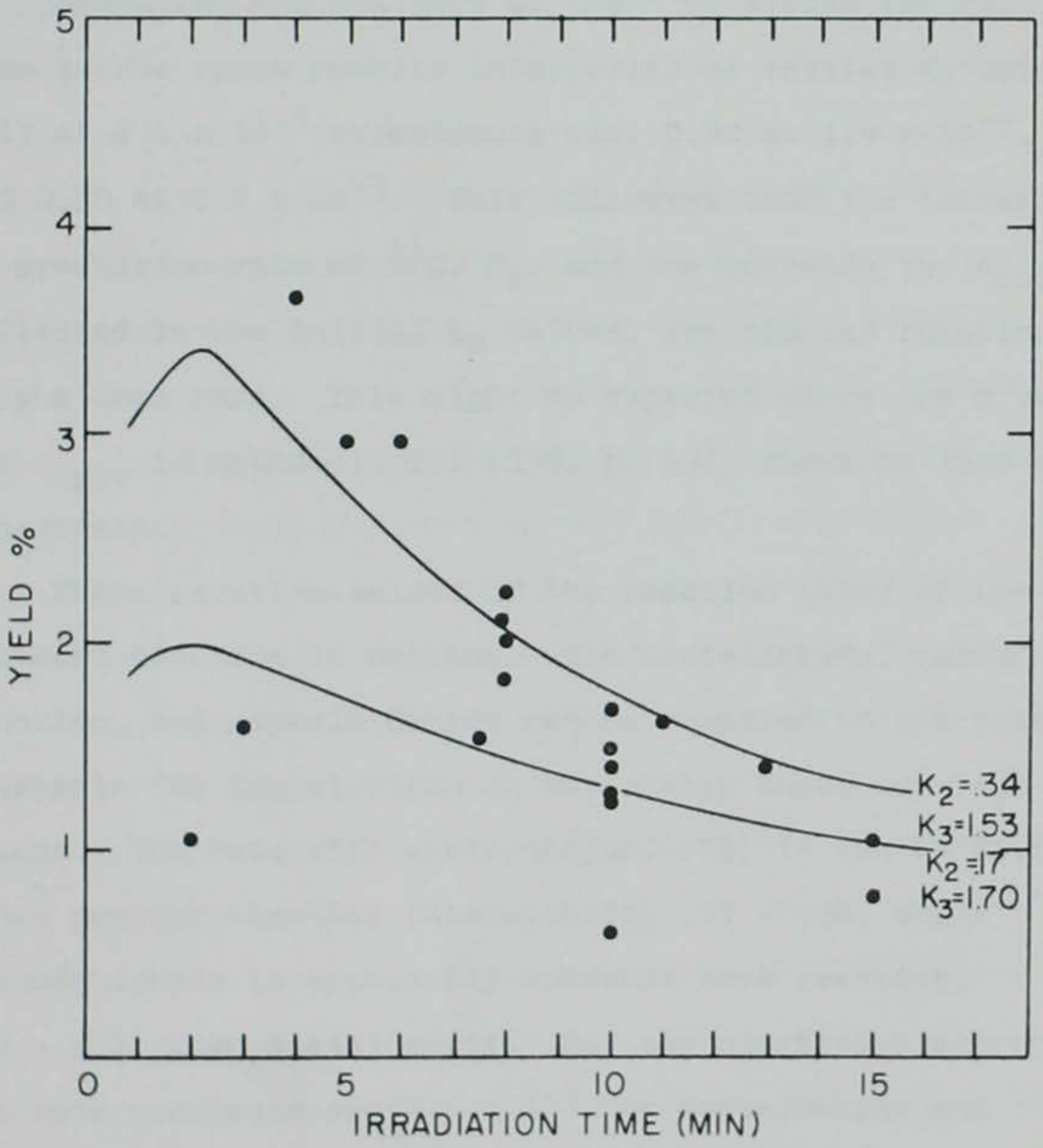


Figure 3. Glycolaldehyde yield and calculated curves

the results are not consistent with the proposed reaction system, but the numerical difference may not be significant in view of the cumulative uncertainties in the analysis.

Repeating the analysis of the ^{11}CO yields for different dose rates results in a series of initial K_2 values; 0.17 at 1.5×10^{-3} eV/molecule·min, 0.20 at 1.9×10^{-3}, and 0.30 at 2.7×10^{-3}. This indicates that the increase in production rate of ^{11}C, R_4, and the increase in $[e^-_{solv}]$, reflected in the initial K_2 values, are similar functions of the dose rate. This might be expected since the G value for e^-_{solv} in methanol, 1.1 (138, p. 39), shows no dose rate dependence.

These relative values of the reaction rates of the solvated electron in methanol with acetaldehyde, carbon monoxide, and glycolaldehyde can be compared to the rate constants for the electron in water with these same compounds. The rate with acetaldehyde, .75, is two to five times greater than the rate with CO, .17 - .34, while glycolaldehyde is apparently somewhat more reactive, 1.5 - 1.7, than acetaldehyde. For the hydrated electron the rate constants are 3.5×10^9 for acetaldehyde and 1×10^9 for carbon monoxide. Glycolaldehyde is expected to be a somewhat poorer electron acceptor (138, p. 74) than acetaldehyde but no aqueous data are available.

2. Methanol-benzene mixtures

The protective effect of benzene in the radiation decompositon of a variety of compounds (140-143) has been extensively studied. The protective effect has sometimes been attributed to energy transfer from excited molecules to benzene which, by virtue of its greater stability, dissipates the transferred energy without decomposition. Most radiation chemists (144, 145) find this energy transfer approach unnecessary and attribute the effect which benzene has on radiolysis yields to radical scavenging. Since the recoil reactions of carbon have been thoroughly studied for both methanol and benzene, and since comparative radiation results are available, an exploratory study of recoil reactions in methanol-benzene mixtures was conducted.

Baxendale and Mellows (110) first reported radiation results from mixtures of methanol and benzene. They reported a linear relationship in the yield of formaldehyde as a function of the volume composition of the mixtures, between its value in methanol and zero in pure benzene. This was attributed simply to dilution effects. The molecular hydrogen yield shows a significant negative deviation from linear behavior from which the reactivity ratio of benzene and methanol toward hydrogen atoms was determined to be 140. The reactivity ratio of e_{aq}^- with these two compounds is also large, ~ 700 (137). Ekstrom and Garnett

(145) reported positive deviations from linearity for several radiation products and attributed these effects to radical scavenging. One group of products, including cyclohexadienyl-methanol and anisole, shows a maximum yield in solutions ~ 15% in benzene which was attributed to reactions of radicals from methanol. The yields of another product group, including cyclohexadiene and phenylcyclohexadiene, have a maximum near 80% benzene. These products are attributed to reactions of radicals from benzene with benzene or methanol molecules. Since methanol is a better source of ·H, the reactions radical + benzene and radical + radical are prevented, resulting in yields of products in this group greater than in benzene alone. Sherman (146) has observed the reactivity ratio of benzene to nitrous oxide toward e^-_{solv} in methanol to be 2.3×10^{-3}. This result compares well with reactions of e^-_{aq} for which the benzene to nitrous oxide ratio is 1.3×10^{-3}.

The results of recoil studies in methanol-benzene mixtures are reported in Table 13. Figure 4 shows the yields of C_1 and C_2 products as functions of the benzene volume fraction. The minor negative deviations from linearity for the hydrocarbon products suggest simple dilution effects tempered with removal of hydrogen atoms by the more reactive benzene decreasing the yields of

Table 13. Product yields from methanol-benzene mixtures

Product	Unscavenged methanol	Mole fr. scavenger 1×10^{-3} I_2
carbon monoxide	12.5 ± 1.7[a]	24.5 ± .30[a]
methane	3.97 ± .20[a]	2.56 ± .09[a]
ethane	.91 ± .15[a]	.70 ± .11[a]
ethylene	9.86 ± .40[a]	8.72 ± .30[a]
acetylene	14.40 ± .75[a]	15.7 ± .7[a]
dimethoxymethane	4.30 ± .20[a]	10.0 ± .3[a]
diacetylene	0.0	0.0
ethanol	9.34 ± .58	4.63
toluene	0.0	0.0
cycloheptatriene	0.0	0.0
allylalcohol	1.80 ± .10	.86
2-methoxyethanol	3.48 ± .38	.92
phenylacetylene	0.0	0.0
unknown #1	0.0	0.0
unknown #2	0.0	0.0
1,2-propanediol	8.34 ± .82	-

[a] Results from Palino (73).

.212 vol. fr. benzene	.071 vol. fr. benzene	.910 vol. fr. benzene	Unscavenged benzene
17.55 ± .60	6.47 ± .06	1.71 ± .18	0.0
2.47 ± .09	.53 ± .18	.25 ± .02	.18 ± .03
.41 ± .05	.06 ± .02	.03 ± .01	0.0
6.97 ± .35	1.84 ± .08	.45 ± .02	0.0
12.68 ± .68	6.97 ±1.31	5.67 ± .30	4.68 ± .14
3.61 ± .41	.89 ± .29	.42 ± .12	0.0
-	-	.77 ± .16	1.58 ± .30
5.50 ± .38	1.04 ± .19	-	0.0
-	3.40 ± .14	3.17 ± .08	2.64 ± .14
2.63 ± .28	3.91 ± .18	3.37 ± .19	3.19 ± .33
1.44 ± .16	.48 ± .04	-	0.0
1.54 ± .19	.60 ± .11	.40 ± .10	0.0
-	1.13 ± .38	2.02 ± .20	1.90 ± .26
.59 ± .14	1.78 ± .23	2.11 ± .26	0.0
1.30 ± .07	3.35 ± .26	3.30 ± .12	0.0
.70 ± .06	.42 ± .03	-	0.0

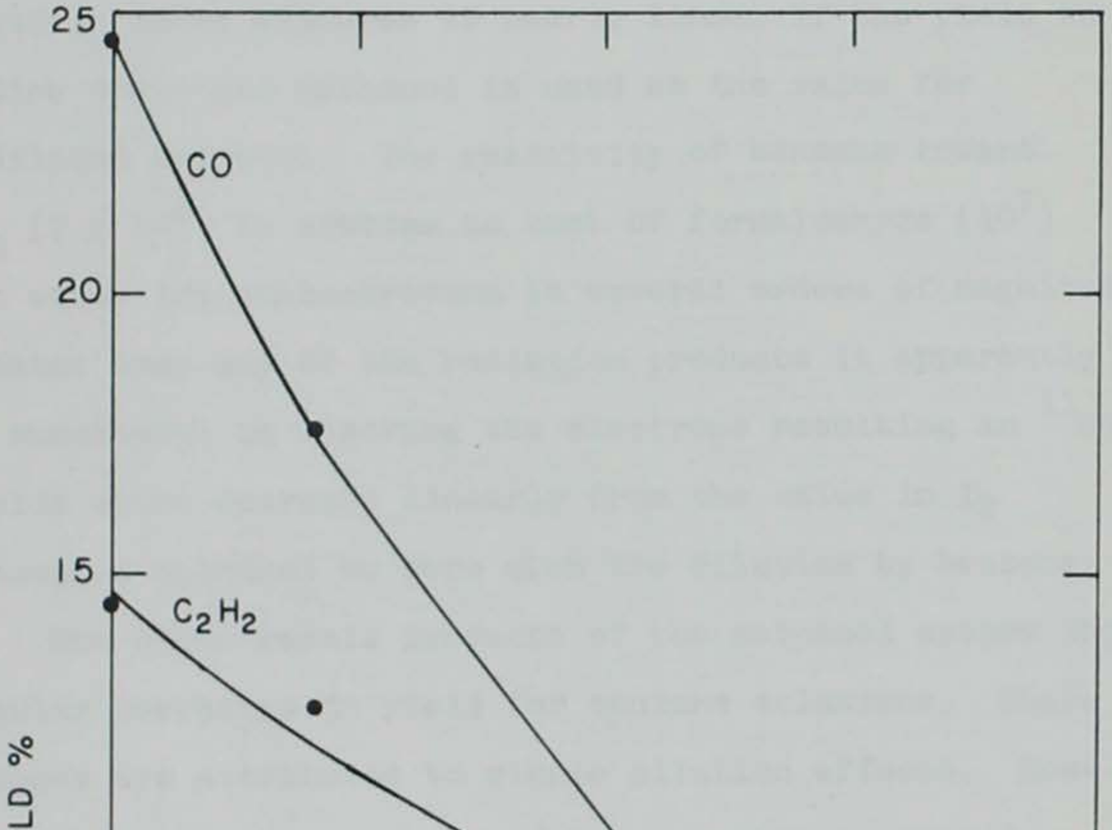


Figure 4. C_1 and C_2 yields in methanol-benzene mixtures

these compounds slightly since their formation depends in part on hydrogen pickup reactions. The carbon monoxide yield in these mixtures is nearly linear if the yield in iodine scavenged methanol is used as the value for undiluted methanol. The reactivity of benzene toward e^-_{aq} (7×10^6) is similar to that of formaldehyde (10^7) but since its concentration is several orders of magnitude greater than any of the radiation products it apparently is successful in removing the electrons resulting in ^{11}CO yields which decrease linearly from the value in I_2 scavenged methanol to zero with the dilution by benzene.

The other recoil products of the methanol system show regular decreases in yield for benzene solutions. These changes are attributed to simple dilution effects. However, some of the products of benzene show increased yields when methanol is added analogous to the results in the radiation studies. The location of the maximum yields of products like toluene and cycloheptatriene cannot be determined from the few data available. Two unidentified products which do not appear in either of the parent systems are reported. They are thought to be simple combination products resulting from labeled fragments from one solvent with a molecule of the other component. Additional studies of methanol-benzene mixtures are required before more definite conclusions can be drawn.

IV. CONCLUSIONS AND SUGGESTED INVESTIGATIONS

Many of the conclusions from the studies presented in this thesis are intimate parts of the discussion sections but some of them will be repeated here with suggested investigations for further clarification.

The recoil reactions of ^{11}C in aromatic compounds produce a wide variety of labeled products. One major reaction is carbon atom insertion into ring and methyl C-H bonds resulting in decomposition of the insertion intermediate to produce labeled C_2 products. The roles of inter- and intra-molecular hydrogen transfer in acetylene formation can be compared using data obtained elsewhere from selectively deuterated compounds. It was shown that ring C-H bonds are somewhat less reactive toward ^{11}C atom insertion than methyl C-H bonds, 0.41 compared with 0.50. Since acetylene is also produced by reaction with the ring C-C bonds (0.37), the ratio of methyl group to ring formed acetylene from toluene is 0.385. Another important reaction with aromatic compounds is carbon atom insertion into C-C bonds of the ring producing a seven-membered ring intermediate which results in the formation of several products including the labeled parent compound. Methylene insertion into the ring C-H bonds of methyl substituted benzenes results in product distributions suggestive of unusually strong electronic and steric effects by the methyl substituents. The study of toluene and p-xylene has extended the range of aromatic compounds subjected to recoil ^{11}C reactions but additional substituted aromatic compounds should give rise to more critical criteria for evaluating the proposed reaction mechanisms. A study of the effects of radiation polymerization on the nature and distribution of ^{11}C labeled products would be another interesting extension of this work.

The study of carbon atom reactions with simple alcohols and ethers led to the formulation of a simple site model for calculating the yields of carbon monoxide from the structure of the oxygen containing molecules. Although the bond counting model is undoubtedly an oversimplification it reflects some interesting characteristics of the deoxygenation reaction. The reaction probability is strongly affected by the availability of electrons at the oxygen site showing an increase with carbon chain branching of adjacent groups. The oxygen atoms of secondary and tertiary alcohols are 20% and 70% more reactive than those of primary alcohols while the oxygens in straight chain ethers are very similar in reactivity to those in primary alcohols. The success of the site model is attributed to the simplicity of the deoxygenation process, possibly a one step direct reaction, and the statistical nature of the reaction which is energetically favored by the strong carbon-oxygen bond formed. Details of the deoxygenation reaction will be difficult to obtain in liquid recoil systems.

The study of ^{11}C reactions in methanol is one of the most complete studies of its kind. The proposed reaction schemes are consistent with product yields determined in dose and scavenger studies and reveal the significance of radiation species in this system. The ability of iodine to change the product distribution by reducing the concentration of radiation species and by trapping ^{11}C labeled intermediates has been discussed. It is unfortunate that the finer details of reaction mechanisms are beyond the scope of current experimental techniques in most recoil studies.

The reactions of the solvated electron in the methanol systems result in time dependent yields of carbon monoxide, acetaldehyde, and glycolaldehyde. Reactions were proposed to account for this dependence through a simple kinetic analysis which determines the relative rates of the electron reactions with these three compounds. A limited number of data were reported for evaluation of dose rate effects suggesting that the solvated electron concentration and ^{11}C production are similar functions of the synchrotron beam intensity. Better control of the beam intensity over a wider range of dose rates would provide the capabilities for more thorough evaluation of the electron reactions and dose rate effects. Such modification of the irradiation facilities are currently in progress.

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